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THE JOURNAL  
—OF THE—  
AMERICAN CHEMICAL SOCIETY.

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VOLUME XVI.

1894.

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HARVEY W. WILEY.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### THE WASTE AND CONSERVATION OF PLANT FOOD.<sup>1</sup>

BY HARVEY W. WILEY.

ONE of the greatest of the practical problems presented for solution by agricultural chemistry is the conservation of plant food. With an abundance of plant food and a favoring climate, it is difficult to place a limit to the power of the earth for supporting life. We have read much in political economy of the limit of subsistence, and one bold philosopher has based a theory of the limitation of the number of human beings upon the earth on the insufficiency of the earth to support a greater number. Happily, however, the Malthusian philosophy was promulgated before the days of that great agricultural renaissance which has been brought about chiefly through the efforts of experimental agricultural chemistry. I am not so blinded by the achievements of agricultural chemistry as to deny to many other branches of science an important and, in many cases, necessary influence in this development of agricultural science; but I think every candid man will admit that in this development chemistry has always taken the front rank and led the way. This is pre-eminently true of the investigations into the nature and extent of the plant food available on the surface of the earth. In this country, owing to the great stores of wealth which the past had accumulated in the soil, it is only within recent years that the question of the supply of plant food has assumed any practical importance. As long as there

<sup>1</sup> Retiring address of the President of the American Chemical Society, Baltimore Meeting, December 27, 1893.

were virgin fields at the disposal of the agricultural rapist, the conservation and restoration of exhausted fields was of little consequence. The result has been that the wealth of hundreds or, perhaps, thousands of years slowly stored in the soil has been poured forth in a century, not only for the enrichment of this country, but for the benefit of all countries. Unfortunately, or fortunately, these stores are now practically explored and there is little left in this land of virgin fertility to tempt the farmer to new conquests. Not only have these stores of plant food been utilized, but, much to the discredit of the American farmer, they have been wasted. The mark of good agriculture is to see fields yielding annually good returns and increasing, or at least not lessening in fertility. This being true, the history of American agriculture to within a few years must be the history of bad farming, for everywhere we have seen fertile fields losing their fertility and farms once productive abandoned. No difference how great the store may be, if it be continually drawn upon and never replenished, the day will some time come when it will be exhausted. This day has come to a large portion of the agricultural lands of this country and to-day there is an awakening everywhere in regard to the best methods of checking the waste and of restoring what has been lost.

I desire for a brief period, on this occasion, to call the attention of the chemists of this country to some of the methods by which plant food is removed from the fields and some of the direct and indirect ways in which it is and may be returned. On a former occasion<sup>1</sup> I have discussed the extent to which plant food is removed from the soil directly in the crops and the dangers which arise to an agricultural community which continually exports its agricultural products. On that occasion I pointed out the amount of potash, phosphoric acid, and nitrogen per acre annually removed by the crops of the United States, and showed that the only safe agricultural products to send out of a country were sugar, oil, and cotton. It is true that with native, unexhausted soils a country may acquire great wealth by agricultural exports, but the history of the world shows that a

<sup>1</sup> Vice Presidential Address before the American Association for the Advancement of Science, Buffalo, 1886.

country which depends for its wealth and its commerce on agricultural exportation is in the end reduced to pauperism. A single example may serve to accentuate this remark; I refer to the island of Cypress, which two thousand years ago was the granary of many cities bordering on the Mediterranean Sea. Supplying hundreds of thousands of people with corn, it gradually became impoverished, and to-day its soils are perhaps the poorest of any known.

The waste to which I desire to call your attention to-day is not that which normally takes place in the production of a crop, but that which is incidental to the cultivation of the soil and to a certain extent unavoidable. My purpose is to develop, if it be possible, the relations of agricultural chemistry to this waste, with the purpose of pointing out a course by which it can be returned and in what way we may at least reduce to a minimum the unavoidable removal of valuable plant food. You have all, perhaps, surmised the character of this waste; I refer to the denudation of fields by water and to the removal of soluble plant food by the percolation of water through the soil.

The losses due to the denudation of fields are purely of a mechanical character. The natural forest, or the natural covering of grass over an area of soil, prevents, to a large extent, the denudation due to heavy downpours of rain. The removal of the forest, and the destruction of the grass by cultivation, leave the soil in a condition in which it is unable to resist the action of flowing surface water. The muddy character of the water in all streams bordering on cultivated hilly fields after a heavy rain storm is a familiar instance of the tremendous energies which are exerted by a heavy downpour of rain in the carrying of the soil into the streams and its transportation towards the sea.

It is not necessary to emphasize the fact that the agricultural chemist is practically powerless to prevent the surface erosion due to heavy rains, but a few practical lessons derived from the application of chemical discoveries to the soils show how, in a certain measure, even surface erosion may be controlled, or at least reduced to a minimum by the application of the principles

of culture founded upon the facts disclosed by advanced science.

The observing agriculturist will have noticed that even in a hilly country a soil *in situ* underlaid by limestone is less likely to be cut up by gullies than a soil similarly situated and deficient in carbonate of lime. The reason of this is plain. In a soil deficient in lime the clays when once brought into suspension by moving water assume a semi-colloid state and remain indefinitely in suspension. Clays, on the other hand, which are heavily impregnated with lime salts are in a flocculated state, and the larger aggregates thus produced settle quickly. The result of this is that such a soil is less easily moved by water, and a field thus treated less exposed to washing by heavy rains.

Our knowledge of flocculation and its physical and chemical results is due largely to the investigations of Shulze, Schloesing, and Hilgard, and the results of their researches have shown in a most emphatic way the beneficial changes which take place, especially in stiff clay soils, by the application of lime.

It is thus an incontrovertible fact that the surface washing of cultivated fields, especially if they be naturally deficient in lime, could be greatly diminished and has been greatly diminished by the free application of this substance.

The change in the physical condition of the soil, which is produced by the lime, is also another important factor worthy of consideration. A stiff clay soil is almost impervious to the penetration of surface water and thus the amount which is carried off is raised to a maximum. A well limed soil, on the contrary, in which the particles are perfectly flocculated, is much more pervious and the amount of water which will be retained and delivered gradually to vegetable growth is much greater. Thus the beneficial effects of lime are manifested in both ways; in the better retention of the flocculated clays and in increasing the capacity of the soil for holding a given amount of water in its interstitial spaces.

There are many other salts which also have the same properties as those of lime, but I have spoken of lime salts chiefly because they are cheaper and, therefore, more economically applied. Perhaps next to lime, common salt would be the most

efficient in producing the results already described; but common salt being extremely soluble would soon be leached out of a soil. On the other hand, lime, even when supplied as hydrate, in which case it is somewhat soluble, quickly becomes converted into a carbonate which is practically insoluble in water which does not contain an excess of carbon dioxide.

I am aware of the fact that liming to prevent erosion by surface drainage has not been emphasized as an example of the benefit of the proper chemical treatment of soils, yet I feel sure that all who will give the subject a thoughtful consideration will agree with me in saying that this aspect of the subject is one of no small importance, especially when considered in respect of hilly fields, and even of fields of more level surface.

Without dwelling long upon this point, it is only necessary to call your attention to the immense quantities of soil material annually conveyed to the sea by the causes of erosion already mentioned to show what an active and powerful foe the farmer has in this source of loss. Anyone who watches, even for a short time, the volume of water carried by the Mississippi into the Gulf of Mexico will have a most effective object lesson in regard to this source of loss.

A more striking lesson may be seen in the hill regions bordering both banks of the Ohio river. Hundreds of fields once covered with sturdy forests of oak, maple, and walnut, and afterwards bearing large crops of maize, tobacco, and wheat, may now be seen furrowed with gullies, as with the wrinkles of age, and abandoned to brush and briers. The same is doubtless true of other hill regions, but I speak the more advisedly of those which have come under my personal observation.

Great, however, as the mechanical loss of plant food is, it is by no means as dangerous as the loss of the soluble materials caused by the percolation of the water through the soil. The study of the nature of the loss of these soluble materials, together with the estimation of their amount, forms the subject of lysimetry. Agricultural chemists have used many devices for the purpose of determining the character and amount of the natural drainage of soils. Evidently the treatment of a specially prepared portion of soil by any solvent, although giving in-

teresting results, does not indicate the natural course of solution. The only way in which this can be determined is to be able to collect, measure and study the character of the drainage from a given portion of the arable surface of the earth *in situ* and under normal conditions. Various methods of lysimetric investigation have been proposed and used, all of them possessing many points of value.

An excellent system of such observation has been established, for instance, at the Agricultural Experiment Station of Indiana. It is not my purpose, however, to discuss the mechanical details of lysimetry, but only to call your attention to the main principles which underlie it. The movement of water near the earth's surface is a matter of especial interest to agriculturists. Whitney<sup>1</sup> has clearly pointed out that the little excess or deficiency of water is of far more importance to the growing crop than the quantity of the excess or deficiency of its other foods. Soils richest in plant food will produce a small harvest if there be a great excess or deficiency of water, while soils which are poor in plant food will produce an abundant crop if the water be present in proper amounts and have proper and timely access to the rootlets of the plant. The study, therefore, of the water movement in the soil, whether laterally, upward, or downward, is of the utmost practical importance. The methods of a study of this kind have been well established by King.<sup>2</sup>

The plant food of the soil, it is well understood, only has access to the absorbent organs of the plant when presented in a proper soluble or semi-soluble form in connection with water. From a chemical standpoint, in connection with the subject under discussion, the movement of water in the soil should be considered in connection, not alone with its power of dissolving plant foods, but with especial reference to its power of carrying them not only away from the reach of the roots of the plant, but even out of the field and into the streams and rivers and eventually into the sea. For our present purpose, therefore, we have only need to examine lysimetric observations for the

<sup>1</sup> "Some Physical Properties of Soils," U. S. Weather Bureau, Bulletin No. 4.

<sup>2</sup> Ninth Annual Report of the Wisconsin Experiment Station, p. 129, et seq.



purpose of determining the kinds of plant food which are most exposed to waste. It is not my purpose to take your time here with a vast array of figures, but I desire only to call your attention to the fact that of the chief plant foods, potash and the nitrates are the ones which are most exposed to loss.

The earliest systematic investigations of the quantity and composition of drainage were commenced at the Rothamsted Station by Lawes and Gilbert<sup>1</sup>, in 1870. Lysimeters were constructed for the collection of the drainage water from thirty, forty, and sixty inches depth of soil, respectively, the soil and subsoil being kept in the natural state of aggregation.

Lawes and Gilbert call attention to the fact that, probably, at the Rothamsted Station, not more than five pounds of nitrogen are secured per acre each year from the atmosphere and the rain-water, while the average loss of nitrogen through the drainage water is over thirty pounds per acre. The quantity, of course, varies with the amount of rain-fall and the activity of nitrification. They speak of the possible exaggeration of the loss of nitrogen on account of the fact that the air had access to the soil both from below and above and therefore the process of nitrification where the lysimeters were placed might have been intensified.

Among the latest researches on this subject are those of Deherain.<sup>2</sup> It is pointed out by this author that the character of the crop grown upon the cultivated field has much to do with the determination of the loss of nitrogen per acre. Those crops which require an immense amount of moisture for their growth, such as the sugar beet, would tend thereby to prevent the loss of nitrogen in the drainage waters, the nitrates being stored in the beet instead of being given up to percolation. In general, it may be said that it is the quantity of the drainage water rather than its richness in nitrates which determines the total loss due to percolation, and from this it may be inferred that the loss by drainage is directly proportional to the rain-fall and inversely proportional to the magnitude of the harvest. The season at which the greatest loss takes place is also, there-

<sup>1</sup> *Jour. Roy. Agric. Soc.*, 27, 241-79 and 311-50; 26, 1-71.

<sup>2</sup> *Annales Agronomiques*, February 25, 1893, pp 65, et seq.

fore, the one in which the growth of the plant is the least vigorous, provided that the vigor of nitrification and quantity of rain-fall remain the same. When plants grow vigorously and when they occupy the soil for a long time, the losses due to drainage are reduced to a minimum. On the other hand, with plants which rapidly ripen, so that the harvest follows soon after the sowing, the losses are greater. The farmer, therefore, who suffers a failure of his crop, not only loses from the smallness of the harvest, but also by the percolation of the water through the soil. For this reason, it is obvious that leaving fields fallow is a very dangerous proceeding. Deherain found that fallow fields during the season lost as high as fifty kilograms of nitrogen per hectare, corresponding to 330 kilograms of nitrate of soda, worth seventy-six francs. These figures show plainly the magnitude of the losses which take place in the one item of nitrogen alone, due to the percolation of rain-water through the soil.

In this connection it may be of interest again to refer to the favorable action of lime in a great many soils in regard to its power of increasing the ability of a soil to hold the soluble plant foods against their removal by water. This favorable action is particularly manifested in many soils in the power of lime to increase their capacity for holding potash.

Warington explains this action of the lime salts, especially the carbonate, by suggesting that by combining with the acids of certain salts, as the carbonates, sulphates, chlorides, and nitrates, they allow the bases of these salts to unite with the hydrated metallic oxides. The carbonate of lime also converts the soluble acid phosphates, applied in manure, to the sparingly soluble calcium phosphates, which, as they gradually enter into solution are converted into ferric and aluminic phosphates. An admirable description of the absorptive power of soils has been given by Warington<sup>1</sup> and many other authors have also discussed this matter in detail.

We can see from the data given above how water continually acts upon a soil in the removal of certain soluble plant foods. It might be inferred from this that all arable soils exposed con-

<sup>1</sup> "Practice with Science," 2.

tinually to rains would soon be exhausted of all valuable, soluble plant food. But it has also been pointed out how certain constituents of the soil have a faculty of absorbing and retaining materials which are soluble in water under ordinary conditions. It must not be forgotten also that the rain-water which descends upon the earth is not pure. Rain-water brings to the earth a certain amount of valuable plant food. Not only does it absorb and hold in solution ammonia and nitric acid, which may be formed by the electrical discharges in the air, but it also collects and brings to the surface of the earth vast quantities of meteoric dust containing valuable fertilizing principles. Thus we have constantly entering the soil water which contains more or less of the materials necessary to plant growth. Even the drainage waters, which leave an arable field, may not reach the sea without giving up much of this material. The drainage waters in passing underneath the earth's surface take devious courses and are often brought near to the surface again or are poured upon soils which are quite different in their texture from those furnishing the materials in solution. Sterry Hunt<sup>1</sup> has pointed out how such waters sooner or later come upon permeable strata by which they are absorbed and in their subterranean circulation undergo important changes. Especially when these waters reach argillaceous strata their content of neutral, soluble salts may suffer great changes. Such waters charged with organic and mineral materials contain usually large amounts of potassium salts and notable quantities of silica and phosphates, and in many cases ammoniated salts, and nitrites or nitrates.

The experiments of Way, Voelcker, and others have shown that in contact with argillaceous sediments these waters give up their potash, ammonia, silica, phosphoric acid and organic matter, which remain in combination with the soil; on the other hand, soda, magnesia, sulphuric acid and chlorine are not removed from the drainage waters. Eichorn attributes this power of selective absorption in the soil chiefly to the action of hydrated double aluminum silicates, and supposes that the process is one of double exchange, equivalents of lime or soda being given up for the potash retained. By this power of

<sup>1</sup> "Chemical and Geological Essays," 95.

selective absorption the mineral matters required for the growth of plants tend to be retained in most soils, while those not required for the growth of plants are removed. Nevertheless, much of the valuable mineral material in solution must escape absorption and finally find its way into the streams, rivers, and seas.

From the foregoing summary of the methods of waste of plant food it has been seen that in spite of all the precautions of the farmer and the chemist, and in spite of the selective absorption of the soil, immense quantities of valuable plant food are carried into the sea, where apparently they are lost to agriculture forever. But this is only an apparent loss. The economies of nature are so happily adjusted as to provide a means of gradually returning in some form or other to the power of the farmer the plant food which has been apparently destroyed. It is true that this return will probably not be to the locality where the waste originally occurred, and it may not take place until after the lapse of thousands of years, but this is of no consequence. Provided arable lands in general receive in some way and at some time a certain return for the plant food removed, it is entirely immaterial whether this be the original plant food removed or other equally as good.

The sea is the great sorting ground into which all this waste material is poured. The roller processes of nature, like the mills of the gods, grind exceedingly slow and small, and the sea becomes the bolting cloth by which the products of milling are separated and sorted out. As soon as this waste material is poured into the sea, the process of sorting at once begins. The carbonate of lime becomes deposited in vast layers, or by organic life is transformed into immense coral formations or into shells. Phosphoric acid is likewise sifted out into phosphatic deposits or passes into the organic life of the sea. Even the potash, soluble as it is, becomes collected into mineral aggregates or passes into animal or vegetable growth. All these valuable materials are thus conserved and put into a shape in which they may be returned sooner or later, to the use of man. In the great cosmic economy there is no such thing as escape from usefulness of any valuable material.

Sterry Hunt<sup>1</sup> has called especial attention to this sifting and sorting power of water and the important part it plays in the formation of crystalline rocks. "Igneous fusion," he says, "destroys the mineral species of the crystalline and brings them back as nearly as possible to the great primary and undifferentiated material. This is the great destroyer and disorganizer or mineral as well as of organic matter. Subterranean heat in our time acting on buried aqueous sediments destroys carbonates, sulphates, and chlorides, with the evolution of acidic gases and the generation of basic silicates and thus repeats in miniature the conditions of the anteneptunian chaos.

"On the other hand each mass of cooling igneous rock in contact of water begins anew the formative process. The hydrated amorphous product palagonite, is, if we may be allowed the expression, a sort of silicated protoplasm and by its differentiation yields to the solvent action of water, the crystalline silicates which are the constituent elements of the crenitic rocks, leaving at the same time a more basic residuum abounding in magnesia and iron oxide and soluble not by crenitic but sub-aerial action."

Let me call attention, for a few moments, to some of the more important ways, pointed out through the researches of agricultural chemists, in which these waste products are restored. We are inclined to look upon the sea as devoid of vegetable growth, but the gardens of the sea are no less fully stocked with economic plants than the gardens of the land. The sea-weeds of all genera and species are constantly separating valuable materials from the waters of the ocean and placing them again in organic form. Many years ago Forchhammer<sup>2</sup> pointed out the agricultural value of certain fucoids. Many chemists have contributed important data in regard to the composition of these bodies. Jenkins<sup>3</sup> gives analyses of several varieties of sea-weed, showing that in the green state it is quite equal to stall manure. The farmers are said to pay as high as five cents a bushel for it. Goessmann<sup>4</sup> also gives analyses of several varieties of sea-weed.

<sup>1</sup> *Mineral Physiology and Physiography*, 188.

<sup>2</sup> *J. prakt. Chem.*, 1st Series, 38, 388.

<sup>3</sup> Annual Report, Conn. State Exp't. Sta., 1890, 72.

<sup>4</sup> Annual Report, Mass. State Exp't. Sta., 1887, 223.

We are indebted, however, to the reports of Wheeler and Hartwell<sup>1</sup> for the fullest and most systematic discussion of the agricultural value of sea-weeds which has been published. Their interesting and elaborate report was published in January, 1893. Those who are interested in the details of this work can find all known publications on the subject properly arranged, classified, and studied in the publication mentioned. We learn from this publication that sea-weed was used as a fertilizer as early as the fourth century, and its importance for this purpose has been recognized more and more in modern days, especially since chemical investigations have shown the great value of the food materials contained therein.

To show the commercial importance of sea-weed as a fertilizer, it is only necessary to call attention to the fact that in 1885 its value for use as fertilizer in the State of Rhode Island was \$65,044, while the value of all other commercial fertilizers was only \$164,133. While sea-weed, in a sense, can only be successfully applied to littoral agriculture, yet the extent of agricultural lands bordering on the sea is so great as to render the commercial importance of the matter of the highest degree of interest.

It is not my intention here to enter into the discussion of the methods of preparing the sea-weed, the times at which it should be gathered and the best means of applying it to the soil; these matters are all thoroughly discussed by Wheeler and Hartwell in the publication mentioned. As an instance of the value of sea-weed at a point far removed from the Rhode Island coast, I may be permitted to say that near the mouth of the Caloosahatchee river, at the town of Ft. Meyers. I saw the most happy effects produced in intensive culture by the application of sea-weed alone to the sandy soils bordering on this arm of the sea. Dr. Washburn, of the Florida Experiment Station, was conducting the experiments to which I refer and he spoke in the highest terms of the value of the sea-weed in his work. Thousands of tons of this sea-weed are allowed to go to waste annually along these shores, simply because the agriculturist has not been informed in regard to its fertilizing value.

There are many other uses for sea-weed besides the agricul-

<sup>1</sup> Rhode Island Exp't. Sta. Bull. 21.

tural one but in these we are not much interested, except incidentally. Many of the varieties of sea-grass are used for filling mattresses, cushions, etc. Other varieties are burned and their ashes used for the manufacture of soda, iodine, and bromine. The gelatinous portions of sea-weeds become exceedingly hard and elastic upon being dried and have been moulded into various forms as substitutes for horn and shells in making handles for knives, files, and other tools. In the Techno-Chemical receipt book, on page 177, may be found receipts for making artificial ebony from the charcoal obtained from sea-weeds; also for making leather, soap, and glue. For the latter purpose the plants are dried and powdered, extracted with warm water, with or without the addition of alcohol. The solution is allowed to settle at a temperature of 120° F. When cool it forms a jelly which is used for various purposes. The direction is then given for making transparent sea-weed leather, opaque sea-weed leather, sea-weed soap, and sea-weed glue.

No attempt can be made to give the quantities of sea-weed which are annually cast upon the shores of the different continents. Perhaps Rhode Island is no more favored in this respect than any other locality and we have seen the value of the sea-weed which was gathered for agricultural purposes in that State alone. The amount gathered represents only a very small fraction of the amount which was thrown upon the shores. It is easy, therefore, to conclude that the quantities of nitrogen, phosphoric acids and potash annually removed from the seas by the plants living therein are no less great in magnitude than those removed from the land by crops and plants of all kinds.

But sea-weed and other vegetable products of the sea are not the only vehicles in which the plant food in solution in the waters of the ocean may be returned to the uses of man. The animal life of the ocean is not less important than that of the land. In the animal economy of the ocean are gathered, therefore, immense quantities of valuable food material which are thus placed in a condition to be at least in part restored in the form of food. Relatively, phosphoric acid and nitrogen are restored in much greater quantities than potash. The composition of fish in general shows that relatively larger quantities of

phosphoric acid and nitrogen are found than of fat and potash. The chemical composition of the nutritive portion of fishes has been thoroughly investigated by Atwater.

The percentage of phosphoric acid in the flesh of American fishes, in its fresh state, is about one-half of one per cent. In one instance, that of smelt, Atwater found, 0.81 per cent. in the flesh of the fish. In the water-free substance of the flesh the percentage of phosphoric acid in round numbers is 2.5. In the case of the smelt above mentioned it amounted to 5.49 per cent. When it is considered that the bones and other refuse of the fish presumably richer in phosphoric acid than the flesh, were not included in this investigation, the quantity of phosphoric acid in fish is distinctly brought to view.

The quantity of albuminoids in the water-free substance of the flesh of fish is enormously high as compared with that of ordinary foods. In round numbers it may be said to be about 75 per cent. of the total water-free substance. In some cases the albuminous matter, or in other words the protein, makes up almost the whole of the water-free substance as in the case of a brook trout, quoted by Atwater, in which the percentage of protein in the dry flesh was 93.25; and of a perch in which it was 93.33; and of a sea bass in which it was 95.88; and a red snapper in which it was 95.38, and others in which even a higher percentage was reported.

It is thus seen that the ordinary fishes of the ocean collect, especially the two great elements of plant food, phosphorus, and nitrogen.

Oysters and other shell fishes collect not only large quantities of phosphorus and nitrogen, but also larger quantities of carbonate of lime. As has been intimated in another place, it is entirely probable that in earlier times when the sea was richer in phosphoric acid than at present, considerable quantities of phosphate of lime may have been secreted with the carbonate of lime in the shell. At the present time, however, the phosphate of lime has almost or quite disappeared from the matters of which shells are composed.

<sup>1</sup> The Chemical Composition and Nutritive Values of Food Fish and Aquatic Vertebrates, by W. O. Atwater. Report of the U. S. Commissioner of Fish and Fisheries, 1888, 679-868.



While the art of fishing is practiced chiefly for the purpose of gaining human food, yet in many large fishing districts the fish waste becomes valuable fertilizing material. Some kinds of fish, as the menhaden, are, however, collected chiefly for their fertilizing value. The use of fish for fertilizing purposes is not new. A most interesting description of the use of agricultural fertilizers by the American Indians is given by Goode.<sup>1</sup> As long ago as 1875 the value of the nitrogen derived from the menhaden was estimated to be about two million dollars. In the year 1878 it is estimated that 200,000 tons of menhaden fish were captured between Cape Henry and the Bay of Fundy. The oil is first extracted from the fish for commercial purposes and afterward the residue is dried and ground and sold to farmers and fertilizer manufacturers. For a complete history of the menhaden the articles of Prof. G. Brown Goode, in the report of the U. S. Commissioner of Fish and Fisheries for 1877 and 1879, may be consulted.

The honor of teaching the American colonists the use of artificial fertilizers belongs, without doubt, to an Indian named Squanto. In Governor Bradford's "History of Plimouth Plantation" is given an account of the early agricultural experiences of the Plymouth colonists. In April, 1621, at the close of the first long dreary winter "they (as many as were able) began to plant their corne, in which service Squanto (an Indian) stood them in great stead, showing them both ye manner how to set it, and after how to dress and tend it. Also he tould them, axcepte they got fish and set with it (in these old grounds) it would come to nothing; and he showed them yt in ye middle of Aprili, they should have store enough come up ye brooke by which they begane to build and taught them how to take it."<sup>2</sup>

Another account mentioned by Goode of the practice of the Indians in this respect may be found in George Mourt's "Relation or Journal of the Beginning and Proceedings of the English Plantation settled at Plimouth in New England, by certain English Adventurers, both merchants and others, London, 1622." "We set the last spring some twenty acres of Indian corn, and

<sup>1</sup> American Naturalist, 14, July, 1880, No. 7., 473, *et seq.*

<sup>2</sup> Coll. Mass. Hist. Soc., 4th Series, 3, 100, 1856.

sowed some six acres of barley and pease, and, according to the manner of the Indians, we manured our ground with herrings, or rather shads, which we have in great abundance and take with great ease at our doors. Our corn did prové well, and God be praised, we had a good inorease of Indian corn, and our barley indifferent good.'"

Thomas Morton, in his "New England Canaan," London, 1632, wrote of Virginia: "There is a fish (by some called shadds, by some, allizes,) that at the spring of the yeare passe up the rivers to spawn in the pond, and are taken in such multitudes in every river that hath a pond at the end that the inhabitants dounge their ground with them. You may see in one township a hundred acres together, set with these fish, every acre taking 1,000 of them, and an acre thus dressed will produce and yield so much corn as three acres without fish; and (least any Virginea man would inferre hereupon that the ground of New England was barren, because they use more fish in setting their corne, I desire them to be remembered, the cause is plaine in Virginea) they have it not to sett. But this practice is onely for the Indian maize (which must be set by hands), not for English grain; and this is, therefore, a commodity there."

The following amusing study quoted by Goode is taken from the records of the town of Ipswich, May 11, 1644:

"It is ordered that all the doggs for the space of three weeks from the publishing hereof, shall have one legg tyed up, and if such a dog shall break loose and be found doing harm the owner of the dogg shall pay damage. If a man refuse to tye up his dogg's legg, and hee bee found scraping up fish in a cornfield, the owner thereof shall pay twelve pence damage beside whatever damage the dogg doth. But if any fish their house lotts and receive damage by doggs, the owners of these house lotts shall bear the damage themselves."

The practice of using fish, therefore, for fertilizing purposes, is many centuries old, but until recent years the farmers residing along the coast were the only ones who received any benefit therefrom; but since the more careful scientific study of the value of fish fertilization, the nitrogenous elements taken from

<sup>1</sup> Coll. Mass. Hist. Soc., 2nd Series, 9, 1832, 60.

the sea by the fish now find their way not only to the gardens and truck farms along the New England and New Jersey coasts but also to the wheat fields of Ohio and the cotton fields of North Carolina.

*Conservation of Nitrogen.*—Attention has been called to the manner in which the nitrogen carried into the ocean by the waste of the land is returned in great part through the marine, vegetable, and animal life. Immense quantities of waste nitrogen, however, are further secured, both from sea and land, by the various genera of birds. The well-known habits of birds in congregating in rookeries during the nights, and at certain seasons of the year tends to bring into a common receptacle the nitrogenous matters which they have gathered and which are deposited in their excrement and in the decay of their bodies. The feathers of birds are particularly rich in nitrogen, and the nitrogenous content of the flesh of fowls is also high. The decay therefore, of remains of birds, especially if it take place largely excluded from the leaching of water, tends to accumulate vast deposits of nitrogenous matter. If the conditions in such deposits are favorable to the processes of nitrification, the whole of the nitrogen, or at least the larger part of it, which has been collected in this débris, becomes finally converted into nitric acid and is found combined with appropriate bases as deposits of nitrates. The nitrates of the guano deposits and of the deposits in caves arise in this way. If these deposits are subject to moderate leaching the nitrate may become infiltrated into the surrounding soil, making it very rich in this form of nitrogen. The beds and surrounding soils of caves are often found highly impregnated with nitrates.

While for our purpose, deposits of nitrates only are to be considered which are of sufficient value to bear transportation, yet much interest attaches to the formation of nitrates in the soil even when they are not of commercial importance.

In many soils of tropical regions not subject to heavy rain-falls, the accumulation of these nitrates is very great. Müntz and Marcano<sup>1</sup> have investigated many of these soils to which attention was called first by Humboldt and Boussingault.

<sup>1</sup> *Compt. rend.*, 101, 1885, 65, et seq.

They state that these soils are incomparably more rich in nitrates than the most fertile soils of Europe. The samples which they examined were collected from different parts of Venezuela and from the valleys of the Orinoco as well as on the shore of the Sea of Antilles. The nitrated soils are very abundant in this region of South America where they cover large surfaces. Their composition is variable, but in all of them carbonate and phosphate of lime are met with and organic nitrogenous material. The nitric acid is found always combined with lime. In some of the soils as high as thirty per cent. of nitrate of lime have been found. Nitrification of organic material takes place very rapidly the year round in this tropical region. These nitrated soils are everywhere abundant around caves, as described by Humboldt, caves which serve as the refuge of birds and bats. The nitrogenous matters, which come from the decay of the remains of these animals, form true deposits of guano which are gradually spread around, and which, in contact with the limestone and with access of air, suffer complete nitrification with the fixation of the nitric acid by the lime.

Large quantities of this guano are also due to the débris of insects, fragments of elytra, scales of the wings of butterflies, etc., which are brought together in those places by the millions of cubic meters. The nitrification, which takes place in these deposits, has been found to extend its products to a distance of several kilometers through the soil. In some places the quantity of the nitrate of lime is so great in the soils that they are converted into a plastic paste by this deliquescent salt.

It is suggested by the authors that the co-existence of the nitrate and phosphate of lime is sufficient in all cases to demonstrate the organic origin of the nitric acid. It would not be possible to attribute such an origin to the nitrate present in these soils if it could not be determined that it was thus associated with phosphate and other remains, the last witnesses of a former animal life.

As a result of the observations of Müntz and Marcano, they conclude that it is not proper to accredit to the electrical discharges in the atmosphere the origin of the nitric acid forming

these deposits although they admit primarily the source of the nitric acid may have been due to electricity, but that it first was passed through the organism of the plant and thence into that of the animal whence it is accumulated in the deposits referred to.

The theory of Müntz and Marcano in regard to the nitrates of soils, especially in the neighborhood of caves, is probably a correct one, but there are many objections to accepting it to explain the great deposits of nitrate of soda which occur in many parts of Chile. Another point, which must be considered also, is this: That the processes of nitrification can not now be considered as going on with the same vigor as formerly. Some moisture is necessary to nitrification, as the nitrifying ferment does not act in perfectly dry soil, and in many localities in Chile where the nitrates are found it is too dry to suppose that any active nitrification could now take place.

The existence of these nitrate deposits has long been known. The old Indian laws originally prohibited the collection of the salt, but nevertheless it was secretly collected and sold. Up to the year 1821, soda saltpeter was not known in Europe except as a laboratory product. About this time the naturalist, Mariano de Rivero, found on the Pacific coast, in the Province of Tarapacá, immense new deposits of the salt. Later the salt was found in equal abundance in the Territory of Antofogasta and further to the south in the desert of Atacama, which forms the Department of Taltal.

At the present time the collection and export of saltpeter from Chile is a business of great importance. The largest export which has ever taken place in one year was in 1890, when the amount exported was 927,290,430 kilograms; of this quantity 642,506,985 kilograms were sent to England and 86,124,870 kilograms to the United States. Since that time the imports of this salt into the United States have largely increased.

According to Pissis<sup>1</sup> these deposits are of very ancient origin. This geologist is of the opinion that the nitrate deposits are the result of the decomposition of feldspathic rocks; the bases thus

<sup>1</sup> A most interesting article on the subject may be found in *Jour. Roy. Agric. Soc.*, 1852, 13, 349, et seq.

<sup>2</sup> Fuchs and De Launy, *Traité des Gîtes Minéraux*, 1893, 1, 425.

produced gradually becoming united with the nitric acid provided from the air.

According to the theory of Nöllner<sup>1</sup> the deposits are of more modern origin and due to the decomposition of marine vegetation. Continuous solution of soils beneath the sea gives rise to the formation of great lakes of saturated water, in which occurs the development of much marine vegetation. On the evaporation of this water, due to geologic isolation, the decomposition of nitrogenous organic matter causes generation of nitric acid, which, coming in contact with the calcareous rocks, attacks them, forming nitrate of calcium, which, in presence of sulphate of sodium, gives rise to a double decomposition into nitrate of soda and sulphate of calcium.

The fact that iodine is found in greater or less quantity in Chile saltpeter is one of the chief supports of this hypothesis of marine origin, inasmuch as iodine is always found in sea plants and not in terrestrial plants. Further than this, it must be taken into consideration that these deposits of nitrate of soda contain neither shells nor fossils, nor do they contain any phosphate of lime. The theory, therefore, that they were due to animal origin is scarcely tenable.

Lately extensive nitrate deposits have been discovered in the U. S. of Columbia.<sup>2</sup> These deposits have been found extending over thirty square miles and vary in thickness from one to ten feet. The visible supply is estimated at 7,372,800,000 tons, containing from 1.0 to 13.5 per cent. of nitrate. The deposits consist of a mixture of nitrate of soda, chloride of soda and sulphate of calcium, sulphate of alumina, and insoluble silica. It is thought that the amount of these deposits will almost equal those in Chile and Peru.

*Phosphatic Deposits.*—Gautier<sup>3</sup> calls attention to the fact that the oldest phosphates are met with in the igneous rocks, such as basalt, trachyte, etc., and even in granite and gneiss. It is from these inorganic sources, therefore, that all phosphatic plant food must have been drawn. In the second order in age

<sup>1</sup> El Salitre de Chile, René F. Le Feuvre y Arturo Dagino, 1893, 12.

<sup>2</sup> Bureau of American Republics, *Monthly Bulletin*, December, 1893, 18, et seq.

<sup>3</sup> *Compt. rend.*, 116, 1271, 6.

Gautier places the phosphates of hydro-mineral origin. This class not only embraces the crystalline apatites but also those phosphates of later formation, formed from hot mineral waters in the jurassic, cretaceous, and tertiary deposits.

These deposits are not directly suited to nourish plants.

The third group of phosphates in order of age and assimilability embraces the true phosphorites containing generally some organic matter. They are all of organic origin. In caves where animal remains are deposited there is an accumulation of nitrates and phosphates.

Not only do the bones of animals furnish phosphates, but they are also formed in considerable quantities by the decomposition of substituted glycerides such as lecithin.

The ammonia produced by the nitrification of the albuminoid bodies combines with the free phosphoric acid thus produced, forming ammonium or diammonium phosphates.

The presence of ammonium phosphates in guanos was first noticed by Chevreul more than half a century ago.

If such deposits overlay a pervious stratum of calcium carbonate, such as chalk, and are subject to leaching, a double decomposition takes place as the lye percolates through the chalk. Acid calcium phosphate and ammonium carbonate are produced. By further nitrification the latter becomes finally converted into calcium nitrate. In like manner aluminum phosphates are formed by the action of decomposing organic matter on clay.

Davidson<sup>1</sup> explains the origin of the Florida phosphates by suggesting that they arose chiefly through the influx of animals driven southward by the glacial period. According to his supposition the waters of the ocean, during the cenozoic period contained more phosphorus than at the present time. The waters of the ocean over Florida were shallow and the shell fish existing therein may have secreted phosphate as well as carbonate of lime. This supposition is supported by an analysis of a shell of *lingula ovalis*, quoted by Dana, in which there were 85.79 per cent. of lime phosphate. In these waters were also many fishes of all kinds and their débris served to increase the

<sup>1</sup> *Engineering and Mining Journal*, quoted in the "Phosphates of America," by Wyatt, 66, et seq.

amount of this substance. As the land emerged from the sea came the great glacial epoch driving all terrestrial animals southward. There was therefore a great mammal horde in the swamps and estuaries of Florida. The bones of these animals contributed largely to the phosphatic deposits. In addition to this, the shallow sea contained innumerable sharks, manatees, whales and other inhabitants of tropical waters, and the remains of these animals added to the phosphatic store.

While these changes were taking place in the quaternary period, the Florida peninsula was gradually rising and as soon as it reached a considerable height, the process of denudation by the action of water commenced. Then there was a subsidence and the peninsula again passed under the sea and was covered with successive layers of sand. The limestones during this process, had been leached by rain-water containing an excess of carbonic acid. In this way the limestones were gradually dissolved while the insoluble phosphate of lime was left in suspension. During this time the bones of the animals before mentioned by their decomposition added to the phosphate of lime present in the under lying strata, while some were transformed into fossils of phosphate of lime just as they are found to-day in vast quantities.

Wyatt<sup>1</sup> explains the phosphate deposits somewhat differently. According to him, during the miocene submergence there was deposited upon the upper eocene limestones, more especially in the cracks and fissures resulting from their drying up, a soft, finely disintegrated calcareous sediment or mud. The estuaries formed during this period were swarming with animal and vegetable life, and from this organic life the phosphates were formed by decomposition and metamorphism due to the gases and acids with which the waters were charged.

After the disappearance of the miocene sea there were great disturbances of the strata. Then followed the pliocene and tertiary periods and quaternary seas with their deposits and drifts of shells, sands, clays, marls, bowlders and other transported materials, supervening in an era when there were great fluctuations of cold and heat.

<sup>1</sup> *Engineering and Mining Journal*, August 23, 1890.



By reason of these disturbances the masses of the phosphate deposits which had been infiltrated in the limestones became broken up and mingled with the other débris and were thus deposited in various mounds or depressions. The general result of the forces which have been briefly outlined, was the formation of boulders, phosphatic débris, etc. Wyatt therefore classifies the deposits as follows:

1. Original pockets or cavities in the limestone filled with hard and soft rock phosphates and débris.
2. Mounds or beaches, rolled up on the elevated points, and chiefly consisting of huge boulders of phosphate rock.
3. Drift or disintegrated rock, covering immense areas, chiefly in Polk and Hillsboro counties, and underlying Peace river and its tributaries.

N. H. Darton, of the U. S. Geological Survey, ascribes the phosphate beds of Florida to the transformation of guano.<sup>1</sup> According to this author two processes of decomposition have taken place; one of these is the more or less complete replacement of the carbonate by the phosphate of lime; the other is a general stalactitic coating of phosphatic material. Darton further calls attention to the relation of the distribution of the phosphate deposits as affecting the theory of their origin, but does not find any peculiar significance in the restriction of these deposits to the western ridge of the Florida peninsula.

As this region evidently constituted a long, narrow peninsula during early miocene times it is a reasonable, tentative hypothesis that during this period guanos were deposited from which was derived the material for the phosphatization of the limestone either at the same time or soon after.

Darton closes his paper by saying that the phosphate deposits in Florida will require careful, detailed geologic exploration before their relations and history will be fully understood.

According to Dr. N. A. Pratt the rock or boulder phosphate had its immediate origin in animal life and the phosphate boulder is a true fossil. He supposes the existence of some species in former times in which the shell excreted was chiefly phosphate of lime. The fossil boulder, therefore,

<sup>1</sup> *Amer. Jour. of Science*, 41, February, 1891.

becomes the remains of a huge foraminifer which had identical composition in its skeleton with true bone deposits or of organic matter.

Perhaps the most complete exposition of the theory of the recovery of waste phosphates, with especial reference to their deposition in Florida, has been given by Eldridge,<sup>1</sup> of the U. S. Geological Survey. Eldridge calls attention to the universal presence of phosphates in sea water and to the probability that in earlier times, as during the miocene and eocene geologic periods, the waters of the ocean contained a great deal more phosphate in solution than at the present time. He cites the observations of Bischof, which show the solubility of different phosphates in waters saturated with carbon dioxide. According to these observations apatite is the most insoluble form of lime phosphate, while artificial basic slag phosphate is the most soluble. Among the very soluble phosphates, however, are the bones of animals, both fresh and old. Burnt bones, however, are more soluble than bones still containing organic matter. Not only are the organic phosphates extremely soluble in water saturated with carbon dioxide but also in water which contains common salt or chloride of ammonium. The presence of large quantities of common salt in sea water would, therefore, tend to increase its power of absorbing lime phosphates of organic origin. It is not at all incredible, therefore, to suppose that at some remote period the waters of the ocean, as indicated by these theories, were much more highly charged with phosphates than at the present time.

According to Eldridge, the formation of the hard rock and soft phosphates may be ascribed to three periods: First, that in which the primary rock was formed; second, that of secondary deposition in the cavities of the primary rock; third, that in which the deposits thus formed were broken up and the resulting fragments and comminuted material were redeposited as they now occur.

"The first of these stages began probably not later than the close of the older miocene, and within the eocene area it may

<sup>1</sup> A preliminary sketch of the phosphates of Florida. By Geo. H. Eldridge, author's edition, 1892, 18, *et seq.*

have begun much earlier. Whether the primary phosphate resulted from a superficial and heavy deposit of soluble guanos, covering the limestones, or from the concentration of phosphate of lime already widely and uniformly distributed throughout the mass of the original rock, or from both, is a difficult question. In any event, the evidence indicates the effect of the percolation of surface-waters, highly charged with carbonic and earth-acids, and thus enabled to carry down into the mass of the limestone dissolved phosphate of lime, to be redeposited under conditions favorable to its separation. Such conditions might have been brought about by the simple interchange of bases between the phosphate and carbonate of lime thus brought together, or by the lowering of the solvent power of the waters through loss of carbonic acid. The latter would happen whenever the acid was required for the solution of additional carbonate of lime, or when, through aeration, it should escape from the water. The zone of phosphate-deposition was evidently one of double concentration, resulting from the removal of the soluble carbonate thus raising the percentage of the less soluble phosphate, and from the acquirement of additional phosphate of lime from the overlying portions of the deposit."

"The thickness of the zone of phosphatization in the eocene area is unknown, but it is doubtful if it was over twenty feet. In the miocene area the depth has been proved from the phosphates *in situ* to have been between six and twelve feet."

The deposits of the secondary origin, according to Eldridge, are due chiefly to sedimentation, although some of them may have been due to precipitation from water. This secondary deposition was kept up for a long period, until stopped by some climatic or geologic change. The deposits of phosphates thus formed in the Florida peninsula are remarkably free from iron and aluminum, in comparison with many of the phosphates of the West Indies.

The third period in the genesis of the hard-rock deposits embraces the period of formation of the original deposits and their transportation and storage as they are found at the present time. The geologic time at which this occurred is somewhat uncertain but it was probably during the last submergence of the peninsula.

In all cases the peculiar formation of the Florida limestone must be considered. This limestone is extremely porous and, therefore, easily penetrated by the waters of percolation. A good illustration of this is seen on the southwestern and southern edges of Lake Okeechobee. In following down a drainage canal which had been cut into the southwest shore of the lake I saw the edge of the basin, which is composed of this porous material. The appearance of the limestone would indicate that large portions of it had already given way to the process of solution. The remaining portions were extremely friable, easily crushed, and much of it could be removed by the ordinary dredging machines. Such a limestone as this is peculiarly suited to the accumulation of phosphatic materials, due to the percolation of the water containing them. The solution of the limestone and consequent deposit of the phosphate of lime is easily understood when the character of this limestone is considered.

Shaler, as quoted by Eldridge in the work already referred to, refers to this characteristic of the limestone and says that the best conditions for the accumulation of valuable deposits of lime phosphate in residual débris appear to occur where the phosphatic lime marls are of a rather soft character; the separate beds having no such solidity as will resist the percolation of water through innumerable incipient joints such as commonly pervade stratified materials, even when they are of a very soft nature.

Eldridge is also of the opinion that the remains of birds are not sufficient to account for the whole of the phosphatic deposits in Florida. He ascribes them to the joint action of the remains of birds, of land and marine animals and to the deposition of the phosphatic materials in the waters in the successive subsidences of the surface below the water line.<sup>1</sup>

*Potash Deposits.*—In the foregoing pages I have tried to set clearly before you the different ways in which the waste of nitrogen and phosphoric acid has been recovered by nature in a form suitable for restoration to arable fields. In the case of potash, however, we have seen that this

<sup>1</sup> For an elaborate discussion of phosphate deposits consult *Giles Mineraux, par Fuchs et DeLaunay*, 309, et seq.

element is not restored by the processes already mentioned, in amounts proportionate to nitrogen and phosphorus. Potash salts, being extremely soluble, are likely to be held longest in solution. Some of them, of course, are recovered in the animal and vegetable life, of which we have spoken, but the great mass of potash carried into the sea still remains unaccounted for. The recovery of the waste of potash is chiefly secured by the isolation of sea waters containing large quantities of this salt and their subsequent evaporation. Such isolation of sea waters takes place by means of geologic changes in the level of the land and sea. In the raising of an area above the sea level there is almost certain to be an enclosure, of greater or less extent, of the sea water in the form of a lake. This enclosure may be complete or only partial, the enclosed water area being still in communication with the main body of the sea by means of small estuaries. If this body of water be exposed to rapid evaporation, as was doubtless the case in past geologic ages, there will be a continual influx of additional sea water through these estuaries to take the place of that evaporated. The waters may thus become more and more charged with saline constituents. Finally a point is reached in the evaporation when the less soluble of the saline constituents begin to be deposited. In this way the various formations of mineral matter, produced by the drying up of enclosed waters, take place.

The most extensive deposits of potash known are those in the neighborhood of Stassfurt, in Germany. The following description probably represents the method of formation of these deposits:<sup>1</sup>

"The Stassfurt salt and potash deposits had their origin, thousands of years ago, in a sea or ocean, the waters of which gradually receded, leaving near the coast, lakes which still retained communication with the great ocean by means of small channels. In that part of Europe the climate was still tropical, and the waters of these lakes rapidly evaporated but were constantly replenished through these small channels connecting them with the main body. Decade after decade this continued, until by evaporation and crystallization, the various salts pres-

<sup>1</sup> Potash, Columbian Exposition, German Kali Works, 3-4.

ent in the sea water were deposited in solid form. The less soluble material, such as sulphate of lime or 'anhydrite,' solidified first and formed the lowest stratum. Then came common rock salt with a slowly thickening layer which ultimately reached 3000 feet, and is estimated to have been 13,000 years in formation. This rock salt deposit is interspersed with lamellar deposits of 'anhydrite,' which gradually diminish towards the top and are finally replaced by the mineral 'polyhalite,' which is composed of sulphate of lime, sulphate of potash, and sulphate of magnesia. The situation in which this polyhalite predominates is called the 'polyhalite region' and after it comes the 'kieserite region,' in which, between the rock salt strata, kieserite (sulphate of magnesia) is imbedded. Above the kieserite lies the 'potash region,' consisting mainly of deposits of carnallite, a mineral compound of muriate of potash and chloride of magnesia. The carnallite deposit is from 50 to 130 feet thick and yields the most important of the crude potash salts and that from which are manufactured most of the concentrated articles, including muriate of potash."

"Overlying this region is a layer of impervious clay which acts as a water-tight roof to protect and preserve the very soluble potash and magnesia salts, which, had it not been for the very protection of this overlying stratum, would have been long ages ago washed away and lost by the action of the water percolating from above. Above this clay roof is a stratum, of varying thickness of anhydrite, (sulphate of lime,) and still above this a second salt deposit, probably formed under more recent climatic and atmospheric influences or possibly by chemical changes in dissolving and subsequent precipitation. This salt deposit contains ninety-eight per cent. (often more) of pure salt, a degree of purity rarely elsewhere found. Finally, above this are strata of gypsum, tenacious clay, sand, and limestone, which crop out at the surface."

"The perpendicular distance from the lowest to the upper surface of the Stassfurt salt deposits is about 5000 feet (a little less than a mile), while the horizontal extent of the bed is from the Harz Mountains to the Elbe River in one direction, and from the city of Magdeburg to the town of Bernburg in the other."

According to Fuchs and DeLauny<sup>1</sup> the saline formation near Stassfurt is situated at the bottom of a vast triassic deposit surrounding the city of Magdeburg. The quantity of sea water which evaporated to produce saline deposits of more than 500 meters in thickness must have been enormous and the rate of evaporation great. It appears that a temperature of 100° would have been quite necessary, acting for a long time, to produce this result.

These authors therefore admit that all the theories so far advanced to explain the magnitude of these deposits are attended with certain difficulties. What, for instance, could have caused a temperature of 100°? The most reasonable source of this high temperature must be sought for in the violent chemical action produced by the double decompositions of such vast quantities of salts of different kinds. There may also have been at the bottom of this basin some subterranean heat such as is found in certain localities where boric acid is deposited.

Whatever be the explanation of the source of the heat it will be admitted that at the end of the permian period there was thrown up to the northeast of the present saline deposits a ridge extending from Helgoland to Westphalia. This dam established throughout the whole of North Germany saline lagoons in which evaporation was at once established, and these lagoons were constantly fed from the sea.

There was then deposited by evaporation, first of all a layer of gypsum and afterwards rock salt, covering with a few exceptions the whole of the area of North Germany.

But around Stassfurt there occurred at this time geologic displacements, the saline basin was permanently closed and then by continued evaporation the more deliquescent salts, such as polyhalite, kieserite, and carnallite, were deposited.

These theories account with sufficient ease for the deposition of the saline masses, but do not explain why in those days the sea water was so rich in potash and why potash is not found in other localities where vast quantities of gypsum and common salt have been deposited. It may be that the rocks composing the shores of these lagoons were exceptionally rich in potash

<sup>1</sup> *Giles Mineraux*, 429.

and that this salt was, therefore, in a certain degree, a local contribution to the products of concentration.

Through the ages of the past, the rich stores of plant food have been steadily removed from arable fields and apparently forever lost. But in point of fact no particle of it has been destroyed. Even the denitrifying ferments described by Springer, Gayon and Dupetit, and Muntz, reduce only to a lower stage of oxidation or restore to a gaseous form the nitric nitrogen on which alone vegetables can feed. But electricity, combustion, and the activity of certain anaerobic ferments herding in the rootlets of legumes and other orders of plants, are able to recover and again make available this loss.

Lately Winogradsky and Warington have shown that an organism can be grown in a sugar solution containing certain salts, and excluding all nitrogenous matter save the free nitrogen of the atmosphere, which is capable of oxidizing and assimilating this inert gas. In a solution containing 7 grams of sugar as high as 14 milligrams of nitrogen have been fixed.

Warington says in speaking of this phenomenon:

"That a vegetable organism should be able to acquire from the air the whole of the nitrogen which it needs, is certainly very remarkable and is an extraordinary fact both to the physiologist and the chemist."<sup>1</sup>

The fact that a few million years may supervene before the particle that is carried off to-day as waste may return to organic life, shows the patience rather than the wastefulness of nature.

As a result of this general review of the migrations of plant food, the reassuring conclusion is reached that there is no danger whatever of the ultimate consumption or waste of the materials on which plants live. Circumscribed localities, through carelessness or ignorance, where once luxuriant crops grew, may become sterile, but the great source of supply is not exhausted. In fact, as the rocks decay and nitrifying organisms increase, the total store of plant food at the disposal of vegetation may continue to grow. When we join with this the fact that the skill of man in growing crops is rapidly increasing, we

<sup>1</sup> *Chem. News*, Oct. 13, 1893, 170.



find no danger ahead in respect of the quantity of human food which may be produced.

Only the novelist might be able, by the aid of an unfettered imagination, to say how many human beings the United States alone will be able to feed in comfort. With the aid of scientific agriculture, with the help of the agricultural chemist we may safely say that a thousand million people will not so crowd our means of subsistence as to make Malthus more than a pleasing theorist. As I pointed out in my vice-presidential address at Buffalo, the death of humanity is not to come from starvation but from freezing, and many a geologic epoch will come and go before this planet dies of cold.

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### A NEW FORM OF AIR-BATH.<sup>1</sup>

BY EWALD SAUER, PH.D.

IN a recent article on the prevalent forms of air-baths, H. Petersen shows<sup>2</sup> conclusively that the designs ordinarily in vogue, whether made from copper or from aluminum,<sup>3</sup> are far removed from the ideal of such an apparatus. The deficiencies are chiefly in the direction of variable temperature and insufficient ventilation for the purpose of rapidly removing the liberated steam. The use of jacketed air-baths, as Soxhlet's apparatus,<sup>4</sup> while providing for constant temperature, limits the range of temperature to the boiling points of the liquids employed, and is subject also to limitations in size.

In order to obviate these difficulties, I have designed an air-bath, which while resembling externally the ordinary forms, differs from them in a few essential points. The main feature is the introduction of two bottoms which are connected with each other by several open tubes. These two bottoms are also joined together in the front and in the rear, while on the sides the space is open. A funnel-shaped opening in the center of the lower bottom allows the flame of an ordinary burner to freely

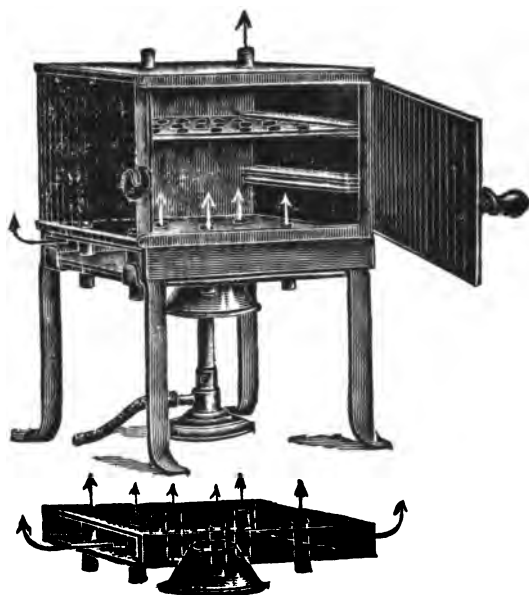
<sup>1</sup> Read before the Cincinnati Section, Oct. 14, 1892.

<sup>2</sup> *Ztschr. angew. Chem.*, 1892, 36.

<sup>3</sup> *Ber. d. chem. Ges.*, 1892, 3637-40.

<sup>4</sup> *Ztschr. angew. Chem.*, 1891, 363-68.

play on the lower surface of the upper or true bottom of the bath.



By means of this disposition the flame and the heated air current pass between the two bottoms about the series of connecting tubes, and issue on both sides. As a result, not only is the upper bottom heated, but also the series of tubes, while through the latter a current of hot air possessing the temperature of the upper bottom enters the interior of the bath. This hot current does double duty. In the first place it maintains a constant temperature in the bath; in the second, it effects a rapid removal of the aqueous vapor, which would be liberated as usual by the simple external heating.

That this device enables the chemist to secure the two desiderata of a constant temperature throughout the interior of the bath, and quick evaporation, is evident from the following tables of experimental results :

TABLE 1.

Force of Bunsen burner flame.	Temperature upper part of air-bath, degrees.	Temperature lower part of air-bath, degrees.
I	220	215
$\frac{1}{2}$	{ 128	127.5
	{ 104.5	104.5
$\frac{1}{4}$	83.5	83

The differences noted above are largely due to the different lengths of the mercury column of the thermometer enclosed in the heated space.

TABLE 2.

Charge.	Temperature when empty.	Lowest temperature observed.	Temperature at close of evaporation.	Duration, minutes.	Grams of water evaporated.	Remarks.
5 grams asbestos and 10 grams water in a glass dish.....	124.5°	111°	120°	15	10	Several experiments with uniform results showed that the location of the charge in the bath did not affect the time required.
	118.5°	111°	115°	40	10	
10 grams water in an aluminum dish....	124°	111°	114°	14	10	Several experiments showed conclusively that as soon as the water was completely evaporated the temperature returned rapidly to that indicated at the beginning.
	103°	96°	102°	14	10	
5 grams milk and 5 grams pumice stone in an aluminum dish....	100.5°	92°	95°	12	5	Slight darkening of the residue.
	85°	82°	85°	15	5	

The end of the operation is readily recognized by the fact that no moisture issues from the upper openings (indicated by an arrow in the diagrams), *i. e.*, a cold beaker held over the openings is not dimmed.

These new air-baths are manufactured from both copper and aluminum by Max Kaehler & Martini, 50 Wilhelmstrasse, Berlin.

## THE CHEMICAL AND PHYSICAL INVESTIGATION OF SOILS.<sup>1</sup>

BY E. W. HILGARD, CALIFORNIA.

I DESIRE to place before this Congress, without going into analytical details which will be set forth in a special report to the Association of Official Chemists, the general results of my long-continued studies on direct soil examination by physical and chemical means that have led me to attach to such examinations a far greater practical importance than is now usually assigned to them by the consensus of opinion both in Europe and America.

I premise that I was led into these investigations more particularly as a consequence of my almost continuous residence in the newer, thinly-settled or unsettled portions of this country, where the question of the fitness of lands for general agriculture, and their special adaptations are burning questions, which are there constantly pressed upon the attention of whosoever occupies a public position in connection with agricultural colleges or experiment stations. My researches have, therefore, borne essentially on virgin soils, or at least such as had been cultivated only for a short time and had received not even incidental fertilization.

With material so different from that which in Europe and in the eastern United States have led most agricultural chemists to consider direct soil examination, and especially chemical soil analysis, as of little practical value, it is not surprising that I should have been led to conclusions differing somewhat widely from those commonly received; so that, while still agreeing that in the case of soils long fertilized, chemical analysis can give but little information as to the immediate producing power, I am satisfied that it can in the case of virgin soils be made of the most direct and vital use to the farmer and intending settler.

The substitute recommended for direct soil examination, after the sweeping condemnation of soil analysis some fifty years ago, was and still is, to put the question to the soil by cultivation and fertilization with the simples, potash, phosphoric acid, and nitrogen; and to deduce therefrom the needs of the soil. It

<sup>1</sup> Read before the World's Congress of Chemists, August 24, 1893.

goes without saying that this is but unpalatable advice to give to a settler in new regions; while even to the farmer in the older countries the carrying-out of a cogent experiment is by no means so easy a task as the precept implies. Moreover, the latter leaves room for great uncertainty in respect to seasonal differences; and the physical peculiarities of the soil are therein left totally out of consideration, although these are just as frequently in fault as the chemical composition, and the farmer is by no means usually to be credited with the ability to determine these points.

In my view, therefore, the examination of soils for the benefit of the agricultural population is one of the most needful, and in the newer states most urgent tasks set before the experiment stations; provided, of course, that the results can be successfully applied to practice.

My attention has from the outset been strongly drawn to the accuracy and certainty with which experienced farmers will, in a region familiar to them, judge of the quality and adaptations of land by its natural vegetation; more particularly by the forest growth. It is obvious that if we could interpret correctly the physical and chemical qualities of soils that have determined the choice of certain plants that occupy them as a result of secular co-adaptation by the survival of the fittest, we should have as definite and much more cogent data than can be supplied us at best by the brief culture experiments we can make. This thought suggested itself to me in noting the invariable recurrence of certain plants on soils showing obvious physical and chemical peculiarities, such as "stiffness" or "lightness" on the one hand, and richness in lime or humus on the other. I therefore determined to test the idea by actual, systematic examination of the soils in all their relations; and it is upon the results of this study, and of their *comparison with actual agricultural practice*, that my views in the premises are based. It need hardly be recalled to mind that, such relations once established, the conclusions flowing therefrom can be legitimately, and as experience shows, fruitfully, projected into cases in which the actual indications of natural vegetation are not available.

The first point requiring attention in such researches is, naturally, the observation of the soils in place, and the recording of all the peculiarities whether of occurrence, structure, derivation, depth, vegetation, local and general climate, and if possible, cultural experience. The taking of the sample to be examined must, of course, be made to conform to the particular conditions of each case, and not to arbitrarily prescribed precepts, above all things. All accidental, abnormal variations must be excluded by a proper selection of the localities, and by sampling the same soil in several places. That it is thus possible to obtain specimens correctly representing in all essentials a wide extent of country without excessive multiplication of samples, my experience has fully proved. The depth to which the "soil" sample should be taken is ordinarily the lower limit of coloration by humus; but should that depth exceed twelve inches, the presumable maximum depth of tillage, one sample should be taken to that depth only. The subsoil is what lies beneath that line of coloration; it is frequently advisable or necessary to sample the soil mass for each twelve inches down to six feet depth, since the nature of the subsoil is one of the most essential points to be observed in all cases.

The first operation I undertake upon any soil sample is to wash about ten grams of it in a beaker with a water current of definite velocity, while stirring actively with a rod. The residue of sand or gravel is examined, macroscopically and microscopically, for the determination of the chief constituent minerals and of their surface condition, whether sharp or much rounded. We thus gain at once a pretty definite estimate of its relations to its place of origin and of its parent rocks, and therefore of its probable general chemical character, it being presumable that the fine matter is of the same general nature as the coarse.

Then follows the "hand test" of the soil by crushing small lumps between the thumb and forefinger, dry at first; then, after wetting, observing the change of color on wetting, and then kneading, in order to test its contents of plastic clay.

The next step, logically, is the test of the relations of the soil to water or moisture. Since the perviousness to water coming from above is so variable according to the accidental condition

and the *modus operandi*, I prefer to determine, as more definite factors, the water capacity and the hygroscopic coefficient, both of which give very definite information in respect to the most essential physical properties of a soil.

In determining the *water capacity* it is quite essential to determine both the *maximum* and the *minimum*, and that in the lowest column of water with which one can operate; I place this at one cm. I use a cylindrical vessel with perforated bottom resembling the "test-lead sieve" of Plattner's blow-pipe chest, of twenty-five or fifty cc. capacity. This is filled with the fine earth, and after weighing placed in a shallow dish with a layer of water. Within about an hour it is saturated to the maximum capacity; it is then weighed, which gives the maximum. Then the wet soil is covered with soil, first air-dry, then with such as has been saturated with moisture, until its weight ceases to decrease by liquid absorption. The last weighing determines the minimum water capacity; the difference between the maximum and minimum indicates the greater or less height to which the soil will raise capillary, liquid water.

The *hygroscopic coefficient*, which contrary to prevailing doctrines I find to be of great importance to the welfare of plants in the arid regions, must be determined by exposing the soil to a fully saturated atmosphere for at least seven hours in a layer 1 mm. thick. Under such conditions, the amount absorbed remains practically the same within ordinary cellar temperatures, contrary to what (according to Knop's law) happens when the air is only partially saturated. We thus obtain a datum which bears a very definite ratio to the clay and humus contents of the soil and its drought-resisting qualities. But in order to obtain comparable results, the drying of the soil must be done at 200° C., for at 100° soils of high absorptive power will continue to lose moisture for weeks. The drying is therefore done in a paraffin bath. From the drying tube or bulb the quantities for the chemical determinations are weighed out.

In the question of the maximum size of grain to be admitted to the chemical analysis, I have also sought to determine by direct experiment the proper limit; instead of assuming an arbitrary one as is usually done, with the result that the chemists of each

country have adopted a different rule, and thus their work is rendered incapable of comparison. Thus the German stations have adopted a two mm. mesh for the fine earth sieve, while the French official rule is "one mesh to the millimeter," leaving the aperture an uncertain quantity because dependent upon the thickness of the wire used. As a matter of fact the aperture is about 0.75 mm. In this country one mm. clear aperture has been adopted by the majority of chemists. Thus it becomes impossible to compare with any degree of certainty the analyses of these different countries.

In 1872, having perfected my apparatus for mechanical soil analysis,<sup>1</sup> I caused an investigation of the question to be made by my assistant, Dr. R. H. Loughridge. The result (see *Am. J. Sci.*, January, 1874) was to show that in the very generalized soil worked upon, seventy-five per cent. of the dissolved soil ingredients was contained in the colloidal clay remaining suspended in water after twenty-four hours, in a column 200 mm. high; and that solution by the hydrochloric acid employed practically ceased when the diameter of 0.025 mm. (0.5 mm. hydraulic value) was exceeded. It was thus apparent that the finest practicable mesh might safely be used for the "fine-earth"; and this I found to be at 0.5 mm. aperture, equal to sixty-four mm. hydraulic value. That for direct comparison by percentages it would be better to come down a much smaller grain-size, is doubtless true; but this degree of fineness would involve elaborate preparations, and difficulties that would render such investigations few and far between. I have, therefore, used the 0.5 mm. mesh in all soil analyses made since under my direction; and as the sieves used in soil work of the surveys of Kentucky and Arkansas were very nearly of the same character, that work remains comparable with mine. But whatever may be the size chosen by any one, the quantitative determination of the grain-sizes of one mm. and two mm. diameter should be made a rule, in order that allowance may be made for them when comparisons are desired.

The preliminary tests made should determine, in a measure,

<sup>1</sup> I omit any detailed reference to this apparatus and the subject of mechanical soil analysis for the reason that the matter has of late had considerable discussion in journals and is presented in full detail in a report to the Association of Official Chemists.



the quantities which it is desirable to use for analysis; since great inconvenience often arises from handling excessive amounts of the iron-alumina precipitate. With such balances and methods as we command at present, I do not think there exists any need of employing hundreds of grams in any ordinary cases. If in the case of ores the selling price is allowed to be governed by the assay of a few grams, it is difficult to see why in the case of a soil we should do otherwise, provided the sample has been well taken and prepared so as to be representative. If that has *not* been done, the taking of fifty grams instead of five will not help the matter much.

I usually weigh out from two and a-half to three grams for general analysis; from three to five for the (separate) determination of phosphoric acid by the molybdate method. When in a strongly clayey soil there is a great deal of calcium carbonate, so much alumina is usually dissolved as to render the handling even from the above amounts troublesome, and parting is best resorted to.

There has been a great deal of discussion in regard to the strength of the solvent to be used in soil analysis. All admit that carbonated water is too feeble to approximate to the assimilative power of plants; while "Aufschliessung" with hydrofluoric acid goes far beyond. It has appeared to me from the outset that we should, if possible, ascertain the possible maximum solvent effect that can be expected of *any* plant; and from the fact that calcium oxalate is of so frequent occurrence in roots, I have thought that oxalic acid might be regarded as the strongest solvent at their command. Now, as is well known, oxalic acid expels from the corresponding salts both hydrochloric and nitric acids. In general, therefore, it stands on a par with these; and it is from this standpoint that I originally determined to use, as the most convenient solvent, hydrochloric acid of medium strength. I have since had the question tested directly by substituting oxalic for hydrochloric acid in comparative analyses of one and the same soil; and while there were differences due to the difficultly soluble compounds formed by oxalic acid, yet the interpretation of the two analyses would, for practical purposes, have been precisely the same.

A series of experiments made by Loughridge in 1873 on one and the same soil with hydrochloric acid of different degrees of concentration showed that the maximum solvent effect was exerted, not by the strongest acid, but by that of about 1.115 sp. gr. I therefore adopted this as the standard acid for soil analysis. Another series of experiments showed that the action was made practically complete by a digestion on the steam bath for five days; this also was, therefore, adopted as the regulation time for the acid digestion, which is always done in a porcelain beaker covered with a watch glass, only half immersed in the steam so as to permit condensation of the acid volatilized. My practice has been to take ten times as many cc. of acid as grams of soil weighed out.

The analysis is then carried out essentially like that of any silicate, including the determination of the silica soluble in sodium carbonate solution, which is a very important datum in estimating the degree of decomposition and zeolite formation that has occurred in the soil. In most cases the silica so determined permits of being assigned to the alumina dissolved, as kaolinite; but to this there are numerous exceptions, there being often twice as much alumina as can be assigned to the silica set free by the acid. The only possible form in which this excess of easily soluble alumina can be present is that of *aluminum hydroxide*; which must, therefore, be considered as one of the normal constituents, notably in the case of highly calcareous, and especially of "alkali" soils.

The phosphoric acid is determined by the molybdate method in a separate and larger portion of material, which is previously ignited in order to determine the "loss by ignition." This latter item, while serving to make the result of the analysis sum up to 100 or thereabouts, is really of no practical significance; since it is made up, besides the combustible matter, of water of hydration from the kaolinite as well as from the various hydrates present, and in calcareous soils of carbon dioxide, which can not be restored by treatment with ammonium carbonate, but must, if necessary, be determined in a separate portion and properly deducted. The combustible portions of the soil farther consist of two distinct portions, namely, humus ready-formed,

and unhumified vegetable matter; so that even if we were able to segregate the water belonging to the several hydrates, we would still be unable to estimate the true humus contents. This can only be done by the method of Grandeau, *viz.*, treatment of the soil first with weak acid and then, after washing, with weak ammonia water, evaporating the filtrate and igniting the residue. The methods of wet or dry combustion usually prescribed for humus determination yield results varying widely with the season, and incapable of serving as the basis of general conclusions; since it is quite uncertain whether or not the unhumified matter will ever become humus, or will be eliminated (as is largely the case in the arid region) by *eremacausis*, or (in the humid region) by fermentation.

In the ash of the humus, at least phosphoric acid should always be determined, since the phosphoric acid thus contained is certainly more available to plants than that not dissolved in the Grandeau treatment, although not as fully so as was at first claimed by Grandeau. The bulk of the humus ash is usually silica, which should be weighed, since we thus gain an idea of the amount of other ingredients contained in the "*matiere noire*." But ordinarily I do not consider a farther prosecution of this analysis as of material practical importance.

The humus percentage gives an approximate idea of the nitrogen store in the soil, the percentage of nitrogen in the "*matiere noire*" being usually three to five per cent. While this is true for the region of summer rains (the "humid"), it seems that in the arid region the nitrogen percentage in the humus is so much greater, that a direct determination alone can serve the purpose. This is readily done by substituting in the Grandeau process a solution of potash or soda for that of ammonia, and after neutralizing the filtrate, evaporating and determining the nitrogen by the Kjeldahl method.

The direct determination of nitrates and ammonia in soils is in my view usually of little interest for general purposes, outside of the arid region, where these compounds remain wholly or partially in the soil and may accumulate to a considerable extent. In the humid region they are usually present in such minute proportions and subject to so much change from day to

day, that for the purpose of judging the soils' general resources in nitrogen such determinations are of little use. When made they should, of course, be done by leaching with water and treatment of the filtrate, since we have no method by which the determination can be made in the whole soil without attacking also the nitrogen of the humus.

The determinations mentioned are in my view all that is usually called for in the examination of soils for practical purposes; very commonly, a general knowledge of the soils of a large region may render a goodly proportion of the determinations unnecessary. Thus the soils derived from the great eruptive sheet of Oregon and Washington have proved to be so universally rich in phosphates, that even this important determination frequently becomes superfluous; and almost the same can be said for potash and lime throughout the arid region. In a large number of cases it is only necessary to identify the soil under examination by mineralogical analysis with others of the same type previously examined from the same region; and this identification naturally carries with it the conclusions previously deduced from observation in the field and laboratory, with very little trouble.

It now remains for me to consider briefly what are the conclusions and practical deductions legitimately flowing from such work as I have outlined. I have heretofore published some detailed discussions of this subject, and will therefore not go into illustrative details, for which I refer to those publications.

What practical meaning shall we attach to the percentage data found by analyses made as described above? How much of each of the important ingredients must be present in order that the soil may be considered "rich" or "poor?"

In this general form the question is unanswerable, as is shown by the comparison of even a very few soils noted for great and lasting productiveness. Manifestly, cultural experience alone can answer the question in *any* form; and it is precisely upon such experience that I have based the general rules I shall enunciate—not *ex cathedra*, but purely as the result of extensive comparisons of the results of chemical analysis of virgin soils with cultural experience.

(1) There is one invariable rule as regards plant-food percentages, to which in virgin soils I fail to find a single exception. It is that all having high percentages are highly productive, unless physical conditions render them uncultivable.

(2) The reverse is by no means generally true, for there are soils having what must be considered very low percentages that nevertheless prove both immediately productive and of considerable durability.

At first blush this admission seems fatal to the claims of chemical soil analysis to practical utility. It certainly proves that such analysis is not to be relied upon, *alone*, to determine the quality of a soil; it must be supplemented by other data than the plant food percentages.

When we discuss the cases forming this class of apparent contradiction, we find, first, that the soils so circumstanced are almost invariably rather coarsely sandy ones, and of considerable depth. So soon as we throw out of consideration the great mass of obviously inert material and examine the "fine earth" corresponding to the grain sizes of rich clay soils, our percentages assume quite a different magnitude, particularly when the great depth to which plant roots can exercise their vegetative functions in pervious soils are taken into consideration. Three other conditions must, however, be fulfilled in order to render such soils of low percentages thrifty; namely, the *ratios* of the several ingredients among themselves must not fall below certain values. In following up the investigation of these ratios, the substance which assumes commanding importance is *lime*. Unless lime is present in sufficient proportional amount to insure the presence of a certain proportion of calcium carbonate at all times, the soil will lack thriftiness; and this is true of all soils, whether of high or low percentages. Moreover, it is strikingly true that the percentage of lime required to fulfill this condition is decidedly higher in clay soils than in sandy ones.

The existence or absence of this important condition is in general readily recognizable by the vegetation characterizing calcareous soils; and one of the first points that must strike the observer is that "lime plants" are, almost throughout, those

upon which old farmers base their successful locations of good land. But in following up this indication we soon find that we must abandon the definition of calcareous soils usually given in text-books ("soils that effervesce with acids"); for all the advantages of calcareous soils are secured with percentages of lime far below those in which the slightest effervescence can be perceived. Here, then, soil analysis renders the essential service of enabling us to account for the choice made by experienced frontiersmen and land experts; practically, *they are in quest of calcareous lands!*

That "a limestone country is a rich country" is an old adage, easily verified by any one who observes the geological map as he travels. But the adage holds true not only of limestone districts, but also of those which from other causes have a notable proportion of lime in their soils. The most striking example of the latter class is the entire arid region, of America as well as of Asia and Africa. As I have more elaborately shown in a special treatise (A Report on the Relations of Soil to Climate; Bulletin No. 3 of the U. S. Weather Bureau), the presence of a notable amount of calcium carbonate in the soils of arid countries is the necessary result of the failure of the scanty rain-fall to leach out the water-soluble products of the weathering process; foremost among these, calcium carbonate is accumulated even where no limestone formations exist. According to the adage above quoted, then, arid countries ought to be rich countries. History shows this to be true, with the proviso that there is any soil at all; for the slowness of the weathering process in arid climates renders soil formation correspondingly slow. Arid climates, moreover, necessitate irrigation; but where, as in Egypt and India, the needful water is supplied, the soil proves almost inexhaustible. It need hardly be mentioned that alongside of lime, other important ingredients accumulate in the soils of the arid regions; notably, *potash* and *nitrates*.

The good results of the presence of much lime in soils, about which there can be no practical question, is doubtless connected partly with the effects which must be attributed to calcium carbonate in the soil as well as in the laboratory: It acts in the "Aufschliessung" of silicates, and it is doubtless from this

cause that (as was mentioned above) we find such large amounts of soluble alumina in calcareous clay soils. Moreover, lime favors *nitrification*, and prevents the formation of injurious *acidity*. That much we can say with certainty; but it has doubtless other important functions, even in a chemical point of view; while as a flocculator of clay it performs a most important physical office, in promoting easy tillage, and circulation of water.

In very sandy soils, as little as 0.10 per cent. of lime may cause the soil to show "lime vegetation;" while in very heavy clay soils, I have known even 0.6 per cent. to be inadequate for this purpose. But apart from the most extreme cases, I find we may safely augur favorably of any soil containing *as much lime as potash*.

The average ratio of the lime percentages of soils in the arid and humid regions I find to be about twelve to one, if we exclude from comparison, on both sides, limestone soils proper. The most general expression I can give to the results of my discussion of the analyses of virgin soils with respect to lime, is that in its presence (in adequate proportions) much smaller percentages of the other plant foods will suffice for high and lasting productiveness; and that much less lime suffices to produce this effect in "light" than in "heavy" soils. It thus appears, then, that the question of the adequacy of plant food percentages is largely dependent upon the proportion of lime, as well as upon the physical character of the soil. The latter point depends essentially, of course, upon the greater facility with which an extended root-development occurs in light than in heavy soils.

I think that the failure of agricultural chemistry to recognize as fully as it deserves the extreme importance of lime in soils, is measurably due to the accidental fact that partly extended limestone formations, partly the prevalence of the mixed glacier drift over the greater part of Europe and Eastern North America, have made calcareous soils so predominant in the regions where agricultural science has been developed, that the exceptional and relatively unimportant non-calcareous areas have escaped attention.

As regards *potash*, the comparisons I have made of hundreds

of analyses from the arid and humid regions of the United States, respectively, show that potash, like lime, accumulates to a remarkable extent in the soils of the arid climates, doubtless in the form of zeolitic compounds; the average proportion in the two regions being about one to three in favor of the arid. Coupled with the fact that there, potash salts are often abundant in the soil water, as well as in the waters of the streams serving to irrigate these lands, the conclusion that potash is not likely to be soon called for as a fertilizer in that part of the continent becomes natural, and is abundantly confirmed by all tests thus far made. The invariable presence of an excess of lime in the arid soils, moreover, promises the current setting-free of potash from the soil zeolites.

The general average of potash in the arid soils is from 0.7 to 0.8 per cent.; for the humid soils of the Cotton States, from 0.21 to 0.25 per cent. No wonder that, considering the frequent deficiency in lime in the latter region, the Stassfurt salts are among the first of the effective fertilizers for the Eastern United States.

As regards *phosphoric acid*, the comparison of the soils of the humid and arid regions fails to reveal any constant difference; its presence in larger or smaller proportions being, apparently, dependent entirely upon local geological and petrographic conditions. It is curious that in my investigations of virgin soils I have been led to the identical figure for the minimum percentage of this substance that will still insure profitable culture, that, I find, has been accepted by European investigators; namely, five-hundredths of one per cent. (0.05 per cent.). When no more than this amount is found to be present in any soil, production will soon cease unless phosphatic fertilizers are used; the duration of profitable culture depending materially, however, upon the proportion of lime present. Anything much above one-tenth of one per cent. usually proves, in virgin soils, to be quite a full supply, rendering the use of phosphates ineffective for a number of years.

Owing to the difficulty formerly existing in the *nitrogen* determination in soils, my investigations in this direction have not been as extended, nor the results as conclusive, as in the case of



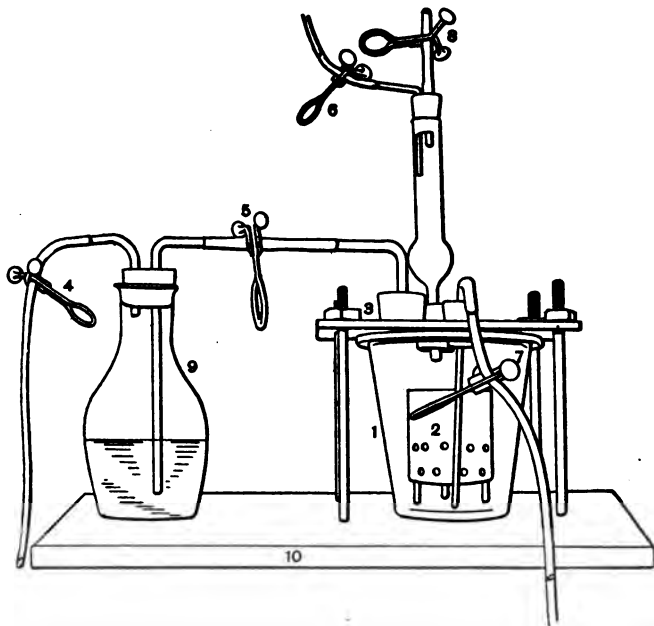
the mineral ingredients. Taking the humus determined according to Grandeau as an approximate gauge of the nitrogen store in soils, it would seem that in the humid region—the Cotton States in particular—less than 0.5 per cent. of humus, estimated to contain say an average of five per cent. of nitrogen, constitutes a deficiency; while in the arid region, as before noted, less than half that amount seems to suffice, rendering the use of nitrate fertilizers ineffective. But owing to the faultiness of the methods employed, the data thus far existing are, as yet, too scanty to serve profitably for the discussion of these points.

In summarizing the outcome of my studies on the relations of the actual productiveness of virgin soils to their plant food percentages, I might say that they support the intrinsically reasonable general thesis that *the amount of available plant food in virgin soils of essentially similar origin is sensibly proportional to the respective totals of such ingredients found by analysis*; provided we take into consideration both the proportions of these ingredients among themselves, and the physical nature of the soil. It is abundantly evident that sandy, pervious soils can, owing to the greater root-development they permit, be fertile with much smaller percentages than those which are difficult of penetration; at the same time, there is an obvious limit beyond which this greater root surface cannot make up for too great a scarcity of one or several ingredients. The test of how far the dilution of a close, fertile soil with pure sand can be carried without detriment to production, is apparently easy to make; and yet these experiments encounter no inconsiderable difficulties in actual execution. Yet their importance is so fundamental that I propose to prosecute them as diligently as circumstances permit, and earnestly hope that others will work in the same line of research.

## HYDROGEN SULPHIDE GENERATOR.

BY H. A. BISHOP.  
Received Nov. 27, 1893.

THE accompanying figure represents a very useful contrivance for the generating of hydrogen sulphide. It consists of 1, an ordinary glass tumbler placed upon a wooden base 10. 2 is a leaden cylinder pierced with small holes. Between



1 and 3 is a rubber washer which makes the generator complete when 1 is held in place by four bolts as seen in the figure, 9 is a wash bottle. When iron sulphide has been placed in 2, the apparatus is ready for generating hydrogen sulphide, first by opening first cock 4, then 5, and finally 6, which allows the acid to enter 1, from a supply receptacle. When the acid has risen above the holes in 2, 6 is closed and all is in operation. After sufficient  $H_2S$  has been obtained 4 is closed first, then 5, and 7 is opened after which 8, which is connected with a water bottle which allows water to wash out what acid remains. The working and construction is very simple.

## THE USE OF ELECTROLYSIS IN TECHNICAL CHEMICAL PROCESSES.<sup>1</sup>

By J. W. LANGLEY, CLEVELAND, OHIO.

**T**ECHNICAL chemistry covers a very wide field stretching from metallurgy on one side to the production of the most delicate colors and odors on the other, in all of which, possibly, electricity is destined to play a part although up to the present time it has only been used to any important extent in the division including the chemical side of metallurgy. Here by far the most notable examples of its use are in the purification of copper and in the extraction of aluminum.

The electrolytic separation of pure copper from crude copper is substantially only a large expansion of the old processes of electrotyping and electroplating, and therefore does not offer much which is novel, but the production of aluminum from its oxide is a typical example of an electro-metallurgical operation. I propose, therefore, to describe somewhat in detail the method employed as it will serve to indicate the steps and precautions to be observed in the applications of electrolysis to other metallic compounds.

The electrolytic production of aluminum is an industry only five years old, but in that short period it has completely revolutionized the manufacture of this metal; indeed it is to-day the only successful method and will probably remain for a long time without a competitor. In this country the process is carried on only by the Pittsburg Reduction Company, at New Kensington, Penna., which manufactures under broad patents granted to Chas. M. Hall, the discoverer and patentee of what is now generally known as the Hall process.

The very important discovery which is the foundation of this method is the fact that oxide of aluminum is soluble in certain double fluorides in a fused condition, the salt which operates the best for this purpose must be composed of fluoride of aluminum and of a fluoride of a base more electro-positive than aluminum; sodium, potassium, and lithium fulfill this condition, but on account of expense fluoride of sodium is preferred. The

<sup>1</sup> Read before the World's Congress of Chemists, August 25, 1893.

mineral cryolite  $\text{Al}_2\text{Na}_2\text{F}_{12}$ , or as it may also be written  $\text{Al}_2\text{F}_6(\text{NaF})_6$ , is a native fluoride coming within the requirements of the class of double fluorides necessary and it forms the principal solvent used. Only, as its melting point is somewhat high, it is an advantage when not operating on a very large scale to add to it small amounts of other fluorides to bring down the fusing point.

Cryolite will dissolve more than twenty-five per cent. of its weight of alumina forming a clear and colorless solution from which the metal can be readily electrolyzed.

There are some features of theoretical interest about this act of solution, for that it is a solution rather than a chemical compound there can be no doubt. Alumina when added to the melted salt dissolves quietly without effervescence or any manifest evolution of heat, resembling in all respects the solution of salt or sugar in water. But alumina is not appreciably soluble in melted sodium fluoride, and aluminum fluoride by itself is infusible except at extremely high temperatures. The presence of both fluorides is absolutely essential. The two fluorides may be taken initially as a double salt or they may be separately mixed with alumina, the final result is the same, *viz.*, the perfect solution of the oxide.

The electrolytic decomposition of the dissolved oxide is carried out on a manufacturing scale by using carbon electrodes. A rectangular vessel made of iron boiler plate is lined with compressed carbon to a thickness of from four to six inches. This constitutes the negative electrode, the positive electrode is formed of carbon rods three inches in diameter by twelve in length, suspended by copper rods from a horizontal copper arm above the iron vessel. The number and disposition of these carbon anodes depends on the scale of the operation. They are hung so that they will terminate about one inch from the carbon lining, and the purpose of suspending them is that they may be easily removable one or two at a time without stopping the whole current going through the apparatus.

The iron vessel is called the pot. The melted cryolite the bath, or when it holds alumina in solution is often termed the electrolyte.

To start the operation some powdered cryolite or the mixture of double fluorides is placed on the carbon lining which is cold. The carbon anodes are then lowered till they make contact with the lining, much local heat being at once produced partly by the resistance of the carbon at the points of contact and partly by numerous short arcs formed where apposition is not perfect. This heat soon melts some of the bath material which flowing between the electrodes adds its own resistance thereby increasing the heat because there is now a larger cross section of conductor and consequently more current carried. In this way the bath material is fused and the pot finally filled. The pot may also be initially charged with melted cryolite ladled into it from a separate melting pot.

During this period while the bath mixture is fusing electrolysis is necessarily going on but it yields only a small quantity of aluminum, probably because of the access of the air and also because any fluorine potentially or actually liberated finds some of the metal in a finely divided and diffused condition with which it reunites.

When a sufficient volume of melted bath is secured the second or permanent stage of manufacture begins, powdered alumina is spread over the top of the bath and periodically stirred down into it. It dissolves almost immediately and normal electrolysis takes place. Aluminum is deposited in a melted condition at the bottom of the bath against the negative electrode, while the oxygen which is transferred to the positive side burns the anodes escaping as carbon monoxide and carbon dioxide. The anodes are thus consumed and must be from time to time pushed down further into the bath. The melted fluorides are not electrolyzed and may be used over and over again indefinitely, it being only necessary to add enough to supply the small losses principally of a mechanical nature occasioned by the removal of the metal. The operation is strictly continuous, alumina is added on the top of the bath and the metal is ladled out from the bottom.

There is quite a complicated adjustment of chemical and electrical forces concerned in the successful electrolysis of alumina which are interesting from the stand point of pure science.

The current employed by the Pittsburgh Reduction Company is 7000 amperes. In order to send this through a bath of melted fluorides only, with the usual current density requires fifteen volts, but as soon as alumina is added the pressure promptly falls to from six to seven volts which is that necessary for the normal working of the process. This E. M. F. is obviously consumed in two ways: First, by the force of polarization necessary to break up a molecule of  $Al_2O_3$ ; second, by the fall of potential due to the resistance of the anodes and of the bath. It is possible to calculate this work both in chemical and in electrical measures.

The heats of formation of one molecule each of the bath constituents is as follows:

Sodium fluoride .....	109,700 calories
Aluminum fluoride .....	550,000 "
Aluminum oxide .....	388,920 "

The electromotive force of decomposition depends, as is well known, on the equivalent and not on the molecular weight and these will be  $Al_2O_3 = Al_2F_6 = 6 (NaF)$ .

The energy of 22,900 calories is proportional to one volt, according to Sir William Thomson, therefore the E. M. F. of decomposition will be:

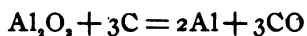
Sodium fluoride .....	$\frac{109700}{22900} = 4.8$ volts
Aluminum fluoride .....	$\frac{550000}{22900 \times 6} = 4.0$ volts
Aluminum oxide .....	$\frac{388920}{22900 \times 6} = 2.8$ volts

Thus the oxide of aluminum is the weakest body present and the only one to be decomposed provided the current density is not permitted to become too great.

The fact that no appreciable quantity of fluorine is given off, but only oxygen, when the pots are working at normal voltage and current is perfectly explained by the above theoretical values of the electromotive force of decomposition. The direct measurement of this force presents considerable difficulty on account of the variation of the resistance of the bath with its temperature, but the best estimates from actual measures show that the breaking stress of one-sixth of a molecule of alumina is certainly less than 3.5 volts. Thus the theoretical number is fairly well sustained by practical observation.

The fundamental conditions for the successful electrolysis of any metallic compound are then these: First, the metallic salt must be in the fluid state; second, if it is rendered fluid by a solvent then the electromotive force of decomposition of the salt must be less than that of the solvent; third, the current density must be carefully regulated. These statements apply equally to aqueous solutions and to baths rendered fluid by fusion. The double fluorides would seem to be the only substances which can fulfill these conditions on a commercial scale for aluminum.

The theoretical equation of the decomposition of alumina by carbon is



which would require about two-thirds of a pound of carbon for each pound of metal produced. Now, in the electrolytic process one pound of carbon anodes is lost for each pound of metal, the slight excess over theory being due to some combustion of the carbon by the air above the surface of the bath. The yield of metal is one pound of aluminum for 18.1 electrical horse power hours. This energy, it must be remembered, is spent both in causing decomposition and in maintaining the temperature of the bath, which is about that of the melting point of copper.

Taking the voltage of the baths as 7, then 18.1 electrical horse power hours represent a continuous flow of 1,926 amperes for one hour. This would theoretically deposit 1.43 pounds of aluminum, so that the actual yield is seventy per cent. of the theoretical ampere production. This must be considered fairly satisfactory. Of course the yield calculated on the total energy consumed is considerably less than this, owing to the large fraction which is turned into heat; but this loss must be set over against the consumption of fuel in ordinary metallurgical work where it is burned solely to produce heat.

Another example of the application of electrolysis to an important industry is the refining of gold and silver, but more particularly silver. The practical details as carried out by the Pennsylvania Lead Company, of Pittsburg, Pa., under the Moebius process are as follows:

Tanks are made and divided into compartments so that they may be connected up in series. The unit compartment is 18" x 24" x 17" deep, and seventy of these are in the circuit at one time. Each compartment has three anodes, 10" x 20" x  $\frac{1}{4}$ ", and four cathodes of about the same area as the anodes. The anodes are composed of the metal to be refined which will average 990 fine in silver, the rest being mainly copper, lead, bismuth with a little gold. The cathodes are thin sheets of pure silver. The surface exposed in each compartment, reckoning both sides of the plates, is twenty square feet, or 1,400 feet for all the tanks. The anodes are hung in a bag to catch the insoluble material which drops from them. The electrolyte is a dilute nitric acid as free as possible from sulphuric acid or chlorine. A current of 180 amperes is used and the voltage required by each compartment is  $1\frac{1}{2}$  volts. The consumption of nitric acid (36° B.) is about two pounds per day for each compartment. The amount of silver deposited is, in practice, about 470 ounces per twenty-four hours in each compartment, which is equal to 1.35 pounds avoirdupois per hour. This includes all interruptions of current for all reasons. The total amount of silver refined per day is 32,900 ounces, or practically one ton. This is eighty-four per cent. of the theoretical yield for 180 amperes working the same length of time without any interruption whatever. The product is practically silver 1000 fine.

The success of this operation depends evidently on the difference of the electromotive force of silver against nitric acid, and of copper, bismuth, and lead against nitric acid, silver being the lowest. But the difference between silver and copper is not great, and a very careful regulation of current density is necessary, which, however, can be attained, making this method one of the neatest applications of electro-metallurgy and one which replaces the tedious cupellations necessary by the older process which has come down from the middle ages.

Another application, which is wholly chemical, has recently been made to the purification of sewage near New York.

Many attempts have been made to produce caustic soda and chlorine, or bleaching compounds, from common salt by electrolysis; but thus far they have not advanced to the stage of



industrial success. One of the chief reasons for this is because no insoluble anode has been discovered, for in strong solutions platinum is dissolved and carbon is oxidized and corroded; but when the liquid is weak this trouble with the anode is considerably lessened. A report by Dr. Cyrus Edson, of the Health Office, New York City, partly reprinted by the *Electrical Engineer*, gives an account of a successful experiment recently made to disinfect the sewage of the village of Brewsters which was finding its way into the city water supply. Mr. Albert E. Wolf proposed to accomplish the purification of the sewage by treating it with electrolyzed sea water. A current of 700 amperes by five volts is delivered to the water as it flows slowly past seven electrodes. Of these, four are carbon, 12" x 12" x 1" thick, while the anodes are copper coated with platinum. The flow of the solution is so limited that the salt water is electrolyzed to the proper degree and then overflows from the tank directly into the sewer. The disinfection is practically perfect. Tests show that this electrolyzed sea water equals in strength a one per cent. solution of chloride of lime. In the matter of cost the treated sea water costs 0.01 cent a gallon, while a one per cent. solution of chloride of lime costs 1.4 cents per gallon, or the sea water costs only  $\frac{1}{140}$  of the lime. Compared with the cost of corrosive sublimate, the latter is one hundred times as expensive for an equal efficiency, while carbolic acid costs from two to three hundred times as much.

Other applications which have been tried and are now on their way to commercial development are: Bleaching fabrics without chlorine by means of electrolyzed acidulated water only, and the tanning of hides.

Seeing that in electrolysis we have a powerful analytic force at work heaping up products of decomposition at each pole, it would be natural to look for some means to utilize the powerful oxidizing and reducing actions of which the electrodes are the foci. This would be to save and turn to useful account the secondary reactions of the cell. A careful study of the conditions under which these secondary actions are a maximum and a minimum can scarcely fail to lead to many applications of the current in technical chemical work where electricity will be

used primarily as an oxidizing or a reducing agent and only secondarily as an agent for electrolytic decompositions.

There is one great desideratum, and that is a cheap insoluble anode. Platinum is too expensive, and carbon will not long withstand oxidation. It is this lack which to-day, among other conditions, prevents electricity from being a rival to the ammonia process of making soda and to the Leblanc process for producing bleaching powder as a by-product, and to its utilization as an oxidizing agent. When the cheap insoluble anode is found it will open a wide door to the applications of electricity to the chemical arts.

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[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 1.]

### THE IODINE FIGURE OF ROSIN.

BY PARKER C. MCILHINEY, PH.B., A.M.

Received December 9, 1893.

IN the analyses of oils, and especially drying oils, one of the most useful tests is a determination of the Hübl number. The iodine figure of rosin, which is a common adulterant of oils, is stated by Benedikt (*Analyse der Fette und Wachsarten*, 171) to be 115.7; Williams (*Chem. News*, 58, 224) gives 115.31 and 114.80 for refined rosin and 112.01 and 113.28 for ordinary. Mills (*Destructive Distillation*, 13) has determined the bromine absorption to be 112.7 per cent., which would correspond to an iodine absorption of about 179. In order to throw some light on the causes of this disagreement, experiments were made to ascertain the effect of different amounts of iodine in excess, different times of absorption and different qualities of rosin.

Five samples were used representing different grades from "W.W." (water-white) rosin to "A" (black).

In the tests made to ascertain the influence of time and of excess of iodine the rosin used was that known as W.W., which is the best grade in the market. The iodine solution used contained twenty-five grams of iodine and thirty grams of mercuric chloride per liter, and the thiosulphate solution 24.8

grams of sodium thiosulphate per liter. The thiosulphate solution was standardized by means of a solution of potassium dichromate made from chemically pure dichromate which had been further purified by several recrystallizations. The tests were made in bottles of 250 cc. capacity, having carefully ground stoppers, such as are used in the assay of silver bullion. The rosin was in each case dissolved in ten cc. of chloroform and the absorption was effected in a dark closet.

The results were as follows :

Quality of rosin.	Quantity, grams.	Excess of iodine in cc. $\frac{N}{10}$ thio-sulphate.	Time of absorption.	Iodine figure.
Water-white .....	0.3030	17.4	2 hours.	142.9
" " .....	0.3017	25.4	2 "	146.4
" " .....	0.3048	33.2	2 "	148.5
" " .....	0.3010	50.2	2 "	152.1
Water-white .....	0.3007	13.35	1 hour.	126.7
" " .....	0.3027	11.6	2 hours.	133.1
" " .....	0.3003	10.5	4 "	142.0
" " .....	0.3023	8.8	8 "	144.8
" " .....	0.3087	11.55	18 "	160.3
" " .....	0.3033	1.9	52 "	172.6
"A" (black) .....	0.3055	20.25	18 hours.	143.6
"E" .....	0.3012	14.2	18 "	156.4
"C" .....	0.3054	13.7	18 "	153.1
"W.G." (window-glass) .....	0.3160	9.7	18 "	164.2
"W.W." (water-white) .....	0.3087	11.55	18 "	160.3

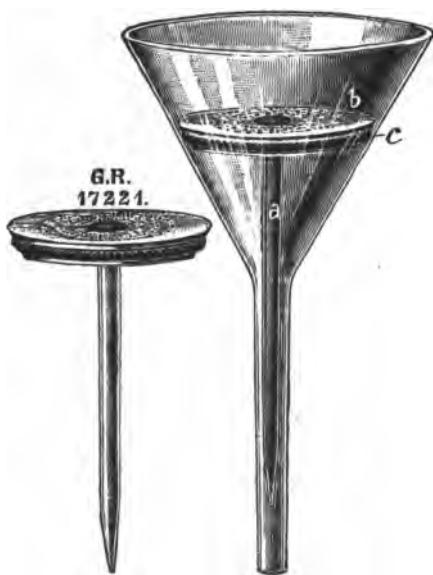
It appears from these results that the average iodine absorption in eighteen hours by different qualities of rosin is 155.5, the average quantity of rosin used being 0.3073 grams and the average excess of iodine equivalent to 13.88 cc.  $\frac{N}{10}$  thiosulphate. The darker samples of rosin absorb less iodine than the lighter ones which have been subjected to less heat. The variations due to different lengths of time and different amounts of iodine in excess are, however, so serious that comparatively little can be learned by Hübl's process as to the nature of an oil when rosin is present in any considerable quantity.

## AN IMPROVED FILTER-DISK.<sup>1</sup>

BY MAX KAEHLER.

**A**N obstacle to the extended use of the porcelain filter-disks, introduced by Otto N. Witt, (*Ber. d. chem. Ges.*, 1886, 918), has existed in the great difficulty of securing a uniformly tight joint between disk and funnel. On the one hand it was necessary to have funnels whose walls were not only perfectly smooth, but were inclined at an angle of exactly 60°. On the other hand any irregularity on the side of the disk seriously affected the tightness of the joint, and frequently, even when the oblique position was scarcely evident to the eye, caused the cracking of the funnel.

These difficulties have been overcome by the introduction of a



modified form shown in the accompanying sketch. The disks are made with a rather deep groove running around the side, in which is held a stout rubber ring (c), projecting a slight distance beyond the adjoining surface. The disk is further perforated in the center by a funnel shaped opening, into which is adjusted a glass rod (a) which extends down into the neck of the funnel. The rubber ring produces a perfect joint while the glass rod keeps the disk in a horizontal position. When large disks and wide necked

funnels are used a cork with channeled sides and fitting closely in the funnel's neck is slipped over the lower end of the glass rod.

<sup>1</sup> Read before the Cincinnati Section, December 15, 1893.

The new device assures rapidity and certainty in manipulation with complete absence of danger to the funnels employed.

These new disks are manufactured by Kaehler and Martini, of Berlin, Germany.

## QUANTITATIVE WORK FOR BEGINNERS IN CHEMISTRY.<sup>1</sup>

By W. A. NOYES.

IN most of our chemical laboratories the work which is given to beginners is chiefly or altogether of a qualitative nature. In many schools and colleges the work begins with a study of the qualitative properties of a series of chemical elements and their compounds, chiefly of gases and metalloids. In other schools the students begin at once with the study of qualitative analysis. A large majority of our students never get beyond this first stage and it is safe to say that they acquire but a very slight knowledge of real chemical work. The work which is done in our scientific and technical laboratories and in chemical factories consists almost entirely of quantitative analyses or of the preparation of chemical substances carried out in an accurate quantitative manner. Indeed, we are accustomed to say that the science of chemistry began with the use of the balance and we all recognize the extreme importance of quantitative relations in most of our chemical work.

We must keep in view several objects in selecting the laboratory work for beginners. First they should become personally acquainted with the appearance and properties of a number of the chemical elements and their compounds. The acquisition of a large amount of knowledge of this kind is desirable but we may easily make the mistake of endeavoring to impart too much. A few topics exhaustively studied will prove of greater value than a superficial study of a great many. This is especially true of qualitative tests with solutions. A beginner can apply a great many such tests in a comparatively short time, but unless his powers of discrimination and of memory are very unusual he will retain only a confused recollection of his work. A second object is to secure a training in delicate and accurate manipulation and in the use of different forms of apparatus. A third

<sup>1</sup> Read before the World's Congress of Chemists, August 26, 1893.

object is to fix in the mind of the student knowledge which may have been imperfectly acquired by watching the demonstrations of a lecturer or by the study of a text-book. Some teachers carry this thought so far that they seem to imply that no knowledge of a topic can be really acquired by the student until he has demonstrated it by personal experiment. Indeed I have heard some teachers contend that they would not allow a text-book in the laboratory, but would have their students acquire all of their knowledge at first hand by their own experiments. Such a principle if logically carried out could never take the student beyond the stage of alchemy, for the student of to-day is no better able to develop a science of chemistry for himself than was the old alchemist. And if you direct his experiments in such a way as to develop and elucidate the science as it is now known, you have forsaken the principle just as much as though a text-book were used.

It seems to me that such views arise from a mistaken conception of the real nature and purpose of laboratory instruction. After all, the method of personal experiment is a very slow and laborious method of acquiring knowledge. Only a very small fraction of our knowledge of a science, if that knowledge is by any means adequate, has been acquired in that way. It is true that the method is absolutely essential for beginners, and I do not think that any of us get beyond the need of it. The man who never uses a balance or handles a test tube will not for very long be a strong factor in the advancement of chemical science. But the method of laboratory instruction is essential, not because knowledge can not be acquired in other ways, but because at the start the imagination of the student is deficient and it is only by means of personal experiments of his own that he can acquire the ability to understand and appreciate the experimental work of others. The memory is also deficient and the personal work on a subject may be of great value for that reason, as well. But the things which we should endeavor to secure in laboratory instruction are, first, such an acquaintance with experimental methods as shall enable the student to thoroughly grasp the solid experimental basis of the science and give him the mental habit of referring everything back to the rigid ex-

perimental test; and second, the ability to do accurate and independent experimental work himself. No student can demonstrate for himself more than an infinitesimal number of experimental facts in comparison with the vast array of such material which has been accumulated.

If the principles which I have suggested are correct we should endeavor to secure as thorough a knowledge as possible of experimental methods, and neatness and accuracy in laboratory technique rather than the illustration of as large a number of details as possible. These results can be secured more fully by a series of quantitative problems than by a large amount of merely qualitative work. I do not mean by this that qualitative work is not necessary and desirable as well, but for the beginners, especially, quantitative work is of more value. In order to make my meaning more clear I will give a few illustrations. One of the earliest problems that I give is the determination of the weight of a liter of hydrogen essentially by Regnault's method. A bulb containing about one-half a liter and bearing a three way cock is exhausted with a Bunsen pump and the residual pressure determined with a manometer. The bulb is then weighed, using a sealed counterpoise of nearly the same volume, then filled with hydrogen, temperature and pressure noted, and weighed again. The results obtained by careful work are usually one or two per cent. too high. A similar determination of the weight of oxygen gives results with a far smaller percentage error. The determination of the amount of oxygen in potassium chlorate by heating about a gram of the salt in a small porcelain crucible placed within a second gives a good illustration of the law of constant proportion. The preparation of potassium perchlorate can be made to furnish a considerable amount of valuable instruction. The capacity of a bottle holding about two liters is determined, a calculation of the amount of potassium chlorate required to give oxygen enough to fill it when only the first stage of the reaction is used, is made and the experiment performed. Then the potassium chlorate and potassium perchlorate are separated and the latter is purified by crystallization. A study of the qualitative reactions which distinguish potassium chloride, potassium chlorate and potassium perchlorate

is made and the tests to establish the purity of the last are applied. Finally a determination of the amount of oxygen in potassium perchlorate gives, in connection with the last problem, an illustration of the law of multiple proportion. I will give but one further illustration—the determination of the relative atomic weights of hydrogen, chlorine, and silver. A known weight of pure silver is dissolved in nitric acid, precipitated with hydrochloric acid and the silver chloride weighed on a Gooch crucible. In a dilute hydrochloric acid the amount of hydrogen is determined by allowing ten cc. of it to act on an excess of zinc in an appropriate apparatus, the hydrogen being measured in a gas burette, accurate corrections being made for temperature, pressure, and aqueous pressure. In another known volume of the same acid the chlorine is determined by precipitation with silver nitrate.

By a careful selection of problems it is possible to give the student, within a reasonable time, practice in the careful use of the more common forms of chemical apparatus. In other words the student can make a beginning at working as a chemist works instead of doing scarcely more than play with bottles and test tubes. Among other advantages of this method of instruction is the fact that the results which are obtained are usually a fairly good criterion by which to judge of the care with which the student has worked, and the student soon finds that careless work will not give good quantitative results. Also the student dwells long enough on a problem so that many details become thoroughly fixed—a result that is rarely obtained in qualitative work, except by means of many repetitions. I am aware that there are some practical difficulties in the way of carrying out the methods which I propose, especially in the matter of apparatus, but these difficulties are not nearly so great as they appear at first sight and I am sure that they are not greater than those which have been overcome in many of our physical laboratories.



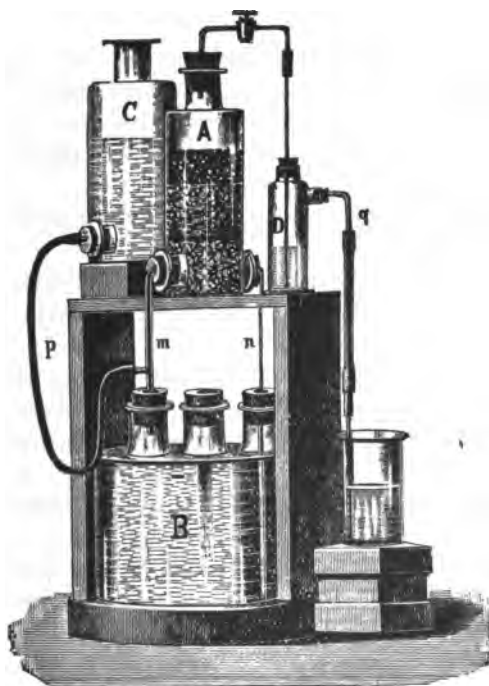
## A NEW HYDROGEN SULPHIDE GENERATOR SPECIALLY ADAPTED FOR USE IN ANALYTICAL LABORATORIES.<sup>1</sup>

BY L. L. DE KONINCK.

**T**HIS new form of generator has yielded such excellent results, especially in connection with quantitative work, where the need of a constant, easily regulated current of hydrogen sulphide is so often felt, that a detailed description of its construction and handling is now made public.

The arrangement of the different parts is shown in the accompanying cut, in which A, the generator proper, rests upon a

wooden support. It consists of a large wide-necked bottle, provided at the lower part with two tubulures, opposite one another. The bottom is covered with a thick layer of broken glass or porcelain. A three-necked Woulff's bottle, B, of ample size, but low form, is placed beneath the wooden support. The tube n passes from A to the bottom of B. The T tube m passes likewise from A to B, but terminates immediately beneath the stopper, while its branch is connected



by means of rubber tubing p, with the tubulure of the movable pressure bottle C. The outlet tube of A, provided with a glass

<sup>1</sup> Read before the Cincinnati Section, November 15, 1893.

cock, enters the wash flask D, from whence gas can be directed at will through q. The middle neck of B can be used for the introduction of a syphon in charging or emptying the apparatus.

The method of using the apparatus is exceedingly simple. A receives a full charge of iron sulphide. B and C are filled with acid, and the latter placed upon a block at the proper elevation. When the cock above A is opened the acid flows into A, the generation of hydrogen sulphide begins, and the gas streams out through the wash bottle D. As ferrous chloride forms in A, its solution on account of its greater specific gravity, sinks continually downward through n, to the bottom of B, while fresh acid enters to take its place. A circulation is thereby established first of strong acid and then of acid containing gradually increasing amounts of ferrous chloride, until the point is reached where nearly the entire stock of acid is changed into ferrous solution. The rapidity of the liberation of the gas can be controlled by raising or lowering C, as well as by the adjustment of the cock in the outlet tube. The current is stopped by lowering C and placing it along side of B, but so that its neck is higher than those of B.

From the above the following advantages of this new apparatus will be easily understood:

1. The current of gas is uniform throughout a given operation, standing under a pressure of 20-30 cm. of water, and capable of being regulated at will.
2. When not in use the pressure is removed and there is no possibility of wasting material either by accident or otherwise.
3. A practically complete utilization of the acid employed is attained.
4. The parts of the apparatus are simple and easy to replace in case of breakage.

It is, of course, evident that the apparatus can be charged with marble or zinc and used to generate carbon dioxide or hydrogen under the same advantageous conditions.

The complete apparatus is constructed in a satisfactory manner by the well-known instrument manufacturers, Max Kaehler and Martini, of Berlin.

## LABORATORY NOTES.

BY JAMES S. DEBENNEVILLE.

Received December 7, 1893.

### BERYL.

In determining the alkalis in a beryl from Fahlun, Sweden, the percentage of potash seemed worth noting. In the analyses of beryl accessible to me I find potash put down as one of the constituent alkalis but undetermined. (J. S. Diller Hillebrands Min. Notes, Bull. 55 U. S. Geol. Survey in the case of a white beryl from Winslow, Me.) F. C. Robinson (*J. Anal. Appl. Chem.*, 6, 510) in a beryl from near Yarmouth, Mass., also notes the presence of phosphoric acid. Beryl from the localities noted in *Dana's Mineralogy*, sixth edition, do not give this alkali. In making the examination the platonic chlorides of cesium (when present) and potassium were boiled with small portions of water until the cesium lines appeared sharply in the spectroscope. The potassium salt was subsequently examined for cesium, with negative results. Other specimens of beryl were then examined and all were found to contain notable quantities of potash. The only contamination appeared to be a little ferric oxide. Nos. I, II, and III, were given to me by the late Dr. F. A. Genth to whose kindness I owe not only the specimens but the constant advice and supervision he gave so freely to those studying under him. No. IV was obtained from Geo. L. English and Co., of New York.

Analyses gave:

I. Fahlun, Sweden, dull yellow. In small grains. Sp. gr. 2.713.

II. Black Mt., Buncombe Co., N. C., apple green. Vitreous. Manganese trace. Sp. gr. 2.748.

III. Acworth, N. H., light green. Vitreous. Sp. gr. 2.714.

IV. Acworth, N. H., light green. Vitreous. Sp. gr. 2.730.

	I.	II.	III.	IV.
SiO <sub>2</sub> .....	64.02	66.24	65.23	66.53
Al <sub>2</sub> O <sub>3</sub> .....	16.44	17.64	17.72	17.11
Fe <sub>2</sub> O <sub>3</sub> .....	0.68	1.36	1.35	0.94
BeO .....	12.91	11.06	12.37	12.24

	I.	II.	III.	IV.
MgO .....	0.23	0.09	0.37	0.20
CaO .....	0.50	0.36	0.61	0.43
K <sub>2</sub> O .....	2.76	0.30	0.35	0.22
Cs <sub>2</sub> O .....	....	....	....	0.12
Na <sub>2</sub> O .....	0.25	0.60	0.53	0.97
Li <sub>2</sub> O .....	0.05	0.14	0.06	0.17
H <sub>2</sub> O .....	1.76	2.06	1.49	1.49
P <sub>2</sub> O <sub>5</sub> .....	0.26	0.78	0.14	trace
	<hr/> 99.86	<hr/> 100.63	<hr/> 100.22	<hr/> 100.45

## COPPER ANALYSIS.

Experiencing considerable trouble in analyzing, for the minor constituents, pig copper and copper alloys high in copper content, a method was sought by which the great mass of the predominant constituent would remain in solution and the elements present only in small quantities would be concentrated in a precipitate of comparatively small bulk and corresponding ease in handling, the use of separate portions of the same sample for the determinations being avoided as far as possible. The method given below is based on a number of experiments conducted with the view of ascertaining the solubilities of the salts involved, under the conditions in which they would occur in analysis of a pig copper and alloy and in analyses of copper containing known quantities of the elements usually found in commercial products.

Ammonia alone being uncertain both in completeness of precipitation and from the tendency of the precipitate to run through the filter, the following modification was adopted for systematic examination of such alloys and was found to remedy the drawbacks above mentioned:

Ten grams of copper were dissolved in nitric acid. Any great excess of acid removed by evaporation. Ammonia added to resolution of the copper salt. Barium hydroxide added in excess of the quantity sufficient to precipitate the minor constituents sought. Excess is quickly indicated by the separation of a scum of barium carbonate. Filtration was made in about half an hour. The precipitate separates out rapidly. Wash well with dilute ammonia to remove any adhering copper salt. With ten grams

of copper and a dilution of 150 cc. but little copper ammonium salts separate out. Fifty grams of copper and a dilution of 500 cc. gave on standing a considerable quantity of the salts. They are, however, readily soluble in dilute ammonia on warming, the precipitate not being appreciably so. On account of the dilution the method is only qualitative for arsenic and phosphorus. For lead, bismuth, tin, iron, manganese, and antimony it is complete. Silver, zinc, and cadmium were removed from the filtrate by decolorizing with solid potassium cyanide and precipitating by hydrogen sulphide. The barium salt gives no trouble. The sulphates of lead and barium can be weighed together. The lead sulphate separated by any of the known solvents, and determined directly or by weighing the residual barium sulphate. The treatment of the precipitate containing lead, bismuth, etc., is a matter of choice.

## PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

*Ore Separators, etc.*—511,512, December 26, Crosby, G. G., magnetic ore separator. 511,162, December 19, Roberts, F. C., puddling furnace. 510,251, December 5, Giroux, J. L., reverberatory, smelting, and refining furnace. 511,476, December 26, Vattier, C., roasting furnace. 511,090, December 19, Mathewson, E. P., furnace tap. 510,223, December 5, Wohlschlegel, C., pottery kiln. 509,890, December 5, Gonder, P., brick kiln. 510,448, December 12, Smith, M. V., coke oven. 510,051, December 5, Seymour, C. E., system of concentrating ores. 510,395, December 12, Ashcroft, E. A., apparatus for generating steam by aid of molten slag. 509,912, December 5, Jory, J. H., amalgamating sluice. 511,334, December 26, Hewett, G. C., manufacture of coke by heating coal at low temperature under pressure, consolidating into lumps, and coking in an ordinary furnace.

*Iron and Steel.*—511,648, December 26, Parkinson, W., converting cast-steel into wrought iron, by mixing charcoal and rolling mill scrap, reducing to spongy mass and mixing with particles of low steel and puddling. 509,973, December 5, Urick, W. P. B., method of casting solid ingots of steel. A rod is thrust into mold, then withdrawn and more molten metal is added to fill the mold. 510,340, December 5, Hines, J. H., coating iron with magnetic oxide, covering first with metal or alloy which will volatilize at a temperature below the fusing point of the iron, and then heating.

*Lead.*—510,979, December 19, Lunge, G., basic lead salts and caustic

alkali. Crude pig lead is oxidized and treated with nitric acid, the silver is precipitated with finely divided lead, and basic lead salts are formed by adding an alkaline carbonate and some free base. The alkaline nitrate is decomposed by ferric oxide, heated air, and steam, and the resulting ferrite is decomposed into ferric oxide and caustic alkali and nitric acid is recovered.

*Copper*.—510,340, December 5, Hines, J. H., ornamenting metal, after cleaning, by depositing copper, or aluminum and enameling.

*Acids and Alkalies*.—510,900, December 19, Cutten, E. B., electrolytic apparatus for soda and chlorine. 511,330, December 26, Fahrig, E., process of and apparatus for obtaining ozone from the air, by absorbing oxygen, releasing the gas from the absorbent, heating, drying, cooling, and passing the electric current. 509,957, December 5, Siepermann, W., manufacture of cyanides; alkaline carbonates are subjected to a dark red heat in presence of ammonia, and potassium cyanide is separated from its aqueous solution by increasing the per cent. of potassium carbonate or caustic potash in solution.

*Sanitary Chemistry*.—510,825, December 12, Stratton, J. L., and Murdock, F., disinfecting apparatus. 510,756, December 12, Adam E., and Reh fuss, M. O., filter, and 510,757, same parties, sterilizing apparatus.

*Brewing and Distilling*.—510,827, December 12, Wiese brock, F. W. A., manufacture of beer. 510,219, December 5, Warren, M., method of and apparatus for beer manufacture. 511,353, December 26, Mosler, J., caramel, from distilling refuse.

*Bleaching and Dyeing*.—511,532, December 26, Kothe, R., *et al.*, blue tetrazo dye. 511,653, December 26, Schultz, G., blue basic dye from alkalinized paradiamins. 509,929, December 5, Moeller M., blue azo dye. 511,688, December 26, Diehl, T., and Moeller, M., blue black tetrazo dye.

*Tanning*.—511,411, December 26, Dennis, M., tanning liquor, normal chromium chloride is rendered basic by adding a solution of an alkali or alkaline carbonate. 511,007, December 19, Zahn, W., tawing hides or skins, a composition of chrome alum and a sulphide of an alkali is used. 511,301, December 19, Lawley, W. F., method for tanning hides.

*Organic Compounds*.—511,303, December 19, Majert, W., piperazine,  $C_4H_{10}N_2$ , anhydrous, with caustic properties, a solvent of uric acid. 511,708, December 26, Moeller, M., amido-naphthol disulphonic acid. 511,450, December 26, Noyes, A. A., and Clement, A. A., paramido-phenol-sulphonic acid, made by electrolyzing a sulphuric acid (conc.) solution of nitro-benzol. 510,617, December 12, Stevens, J. H., and Axtell, F. C., compound of pyroxylin, containing pyroxylin, phenyl acetamide, acetone, and a liquid menstruum. 510,132, December 5, Hagemann, O. C., separating tannin, dissolving tannin from substances containing it in amyl alcohol and separating the alcohol. 511,143, December 19, Higgin, W. H., manufacture of sodium acetate from "esparto liquors," by evaporating water, and treating residue carefully above  $200^{\circ}C$ ., but not high enough to decompose the sodium acetate.

*Oils and Vernishes.*—510,050, December 5, Scollay, G. W., siccatives, formed by adding to a vegetable oil a metallic oxide. 510,734, December 12, Trageser, A. F., apparatus for distilling and concentrating glycerol and heavy oils. 510,672, December 12, Brown, E. G., *et. al.*, "sweet residual petroleum products," purified by passing steam through petroleum while it is boiling for distillation and finally air. 511,051, December 19, Lahusen, J. C., production of neutral wool-grease.

*Plaster and Cement.*—509,924, December 5, Lorenz, J., artificial stone, from "ashes, cinder, burnt sand and cement." 511,735, December 26, Jones, J. K., wall plaster, sugar, 100 parts, flour, 25 parts, air-slaked slime, 250 parts, plaster of Paris, sand, and water. 510,874, December 12, Dutrey, J., artificial emery stones, sulphur, Portland cement, emery, Venetian red, and sugar form the composition. 511,740, December 26, McIlvried, J. R., retarders for plaster, air-slaked lime is kept in an airtight receptacle and mixed with water, flour, liquid glue, and wood ashes and dried.

*Miscellaneous.*—510,421-22-23-24, December 12, Haley, A. E., parchmentized paper board. 509,951, December 5, Schroëder, E., manufacture of metal foil. 510,276, December 5, Lyte, F. M., electrolysis of fused metallic chlorides in a specially devised chamber. 510,834, December 12, Blackmore, H. S., electrolytic process for dissociating soluble salts. 510,065, December 5, Frédureau, J. B. F., composition of matter for crockery ware, consisting of aluminum silicate combined with a soluble alkaline salt and impregnated with fatty or resinous substances. 509,887, December 5, Fischer, J. F., and Peters, O., artificial stone filter, made by heating pulverized silica and glass to a high temperature. 510,376, December 5, Bertrand, P. H., depositing metal upon metal by immersing in solution of soluble salts of metals in dilute sulpho-carbolic acid. 510,013, December 5, Endruweit, C., method of producing metal film and metal paper. 511,271, December 19, Hoskins, Wm., safety paper for checks, made by adding to paper a soluble ferrocyanide and a per-salt of iron, insoluble in water but decomposed by weak acids in presence of a soluble ferrocyanide, and a salt of manganese, decomposed by alkalis or bleaching agents.

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### NEW BOOKS.

DIE SCHMIERMITTEL. METHODEN ZU IHRER UNTERSUCHUNG UND WERTHBESTIMMUNG. Von Josef Grossmann pp. 186. Wiesbaden, 1894. Price M. 4.80.

This treatise is a valuable addition to the literature of lubrication—and while no new methods are described, the bringing together of the various tests, as made use of by the German chemists, simplifies the subject and renders the book one of ready reference.

Especial attention is given to the subject of viscosity—both theoretical and practical—including the “internal resistance” of fluid lubricants. This latter subject has received but little attention in this country, and it is questionable if it is of much practical importance. Eight different viscosimeters are described, not one of which can be considered standard, showing that the same lack of uniformity in determining viscosity exists there as here.

The flash and burning tests are made in a manner similar to methods in use in our railroad laboratories, but the cold test is radically different and liable to error.

Evidently the very complete articles on this subject, by C. B. Dudley and F. N. Pease,<sup>1</sup> have not been consulted by the author. The tests, as formulated by Dudley and Pease, leave little to be desired in the way of accuracy and rapidity in the determination of the value of lubricants used in railroad practice.

The method for estimating rosin oil in mineral oil (Valenta's) could be supplemented by the process described by E. Twitchell (*J. Anal. Appl. Chem.*, 5, 379). A large portion of the treatise is devoted to descriptions of various lubricants for different kinds of machinery.

The author with many years practical experience as chief engineer of the Austrian Northwestern Railroad, gives the results of experiments in this direction, and the reasons for selecting either simple mineral oil or mixed mineral and seed-oil, for special purposes.

This portion of the work will be of value to the manufacturer of compounded oils. The treatise, while in the nature of Engineering Chemistry, is not complete enough in the qualitative reactions of the different oils and fatty acids derived therefrom to enable a chemist to accurately determine seed-oils and animal oils in the presence of each other.

If, however, Dr. Carl Schaedler's work, upon the reactions of fats and oils, be used in connection therewith, the chemist will be amply provided with the reference matter necessary on this subject.

T. B. S.

<sup>1</sup> *The Railroad and Engineering Journal*, 6, 76.



## NOTES.

*Mineral Residues in Sprayed Fruit.*—Dr. R. C. Kedzie, of the Michigan Experiment Station, has examined fruit sprayed with two insecticide mixtures containing copper and arsenic. Strawberries sprayed excessively June 18 and 23 and picked June 24 contained, per pound of fruit, arsenic 0.044 grains, and copper 4.87 grains. Gooseberries sprayed June 18 and 29, July 8 and 22, picked August 2, were washed with hydrochloric acid (ten per cent.) and the washed fruit contained per pound 0.0047 grains arsenic and 0.138 copper. "In these experiments extending through two years, the minerals used in spraying the fruits were found in appreciable quantities in every instance though the amount was small in all cases except where the spraying had been purposely excessive. \* \* \* The use of poisons in horticulture in my opinion is largely in excess of the amount required for a fungicide. One-half or even one-third of the amount usually employed would probably give as good results. \* \* It is safe to refuse all fruits which have been sprayed with these poisons (especially arsenic) during the period of ripening."

It was found that a small part of the poison sprayed upon the surface of the fruit was absorbed into its substance.—*Bulletin, 1911, Michigan Agricultural Exp't. Station, 19.*

*Estimation of Chlorine in Water.*—When the standard silver nitrate solution is employed, with potassium chromate as an indicator, it is often very difficult to decide just when the red color begins to appear, even with the comparison dish of water tinted with the chromate at hand as an aid to the eye. One sufficient reason therefor is that it is hard to compare a clear yellow liquid with one turbid from precipitation of silver chloride.

Following a suggestion of my assistant, Mr. V. H. Gridley, it is now my practice to roughly determine the chlorine present, and then to make a second determination using for comparison 100 cc. of distilled water to which has been added not only the chromate indicator, but also an appropriate amount of standard sodium chloride solution and an amount of silver nitrate solu-

tion just short of that necessary to satisfy the chlorine present. Of course if the chlorine ran so high as to render concentration unnecessary, then 100 cc. of the water itself with the indicator and the partial dose of silver nitrate would be the proper contents for the comparison dish. By these means the eye is greatly aided in noting the slightest appearance of red tint, for in respect of turbidity both dishes are alike. The results are very satisfactory.—*W. P. Mason, Rensselaer Polytechnic Institute, January 20, 1894.*

*The Phenolsulphonic Acid Process for Nitrates in Water.*—The interference of chlorides with this process, resulting in readings decidedly lower than the truth, is well known, but the method of determination is so easy and convenient, that it occurred to me to try the addition of sodium chloride to the comparison standards rather than abandon the process.

The "chlorine" in the water under examination having been previously determined, an appropriate volume of standardized sodium chloride solution is added to each evaporation of standard potassium nitrate solution. Thus the water to be examined, and the nitrate solutions with which it is compared, all contain the same quantity of chlorine. The results are very satisfactory.—*W. P. Mason, Rensselaer Polytechnic Institute, Jan. 18, 1894.*

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### THE BALTIMORE MEETING.

THE Baltimore meeting of the society held December 27 and 28, 1893, was in every respect most successful. This is due in large part to the local committee of arrangements, which in turn expresses itself as under great obligations to Prof. Ira Remsen.

The sessions were held Wednesday, December 27 and 28, 1893, in Prof. Remsen's lecture room in Hopkins Hall, Johns Hopkins University.

Addresses of welcome were made by D. C. Gilman president of the university, and Ira Remsen Prof. of chemistry.

President Gilman, in behalf of the Johns Hopkins University, extended a hearty welcome to the society and offered it all the facilities for its work which the libraries, halls, and laboratories of the university would afford. He referred to a medieval custom, the migration of students from one seat of learning to another, and compared it with the modern and American usage, which transports professors, instead of students, from one point to another. Thus the Christmas and Easter holidays, as well as the long vacation of summer, are now the favorite times for the assembling of literary and scientific associations like that now welcomed to Baltimore.

He then briefly described the buildings of the university, and made an allusion to the many distinguished men of science, from Europe as well as from this country, whose voices have been heard within the walls of Hopkins Hall where this American Chemical Society now holds its annual meeting.

Prof. Remsen in welcoming the society to the chemical lab-

oratory gave a brief account of the way the present building gradually came into being. The laboratory is called Dalton Hall, a name that has a deeper significance than appears at first sight. Dalton was a member of the Society of Friends, and the founder of the Johns Hopkins University and several of those whom he selected to act as trustees of the university were also members of this society. Certainly to every thinking chemist the name of Dalton is a most inspiring one. He gave us some of the greatest thoughts of our science, and laid the foundations of the most profitable speculations in regard to the constitution of matter. His work has been of inestimable value, and has contributed very largely to the advancement of the science of chemistry. The speaker then said that in emphasizing the science of chemistry, as he is very apt to do, he did not wish to be misunderstood. Everyone recognizes the importance of the chemical industries. These need no spokesman. The fact that pure science is not, a mere luxury, but of importance to mankind, is, however, often lost sight of, and it seems desirable that occasionally a voice should be raised in its defence. While this was not necessary on the present occasion, the speaker wished to declare his own attitude, in order, as far as possible, to avoid misunderstanding. Science and industry must go hand in hand. They are mutually dependent. The man of science who speaks with disrespect of the industries is certainly short sighted; and the same is true of the industrial chemist who speaks disrespectfully of science.

In replying to the addresses of welcome the president, Harvey W. Wiley, said that the present membership of the society was 681, of whom 542 had paid all dues. The names added during the year numbered nearly 400. He referred to the valuable work accomplished by the older members and the sacrifices they had made in order that the society might become truly, as well as in name, a national organization. These remarks applied especially to the members of what is now the New York Local Section.

There are now over 4000 professional chemists in the United States, and this allows ample opportunity for enlargement of the membership which is rapidly going on.

We rejoice that there is no longer reason that Americans should go abroad to study chemistry. Facilities equal to those offered abroad are now to be had at the Johns Hopkins University and at other institutions in our own land.

The president then read the annual address which has already been printed in the January issue of this JOURNAL.

G. F. Barker read a memorial of the late Dr. F. Sterry Hunt, at the conclusion of which the members rose to honor his memory.

After a recess of five minutes, Edward Hart was elected secretary pro tempore. The reports of the secretary, treasurer, librarian and editor were then read and adopted.

The treasurer's report follows :

#### TREASURER'S REPORT.

##### RECEIPTS.

Balance on hand, January 1st 1893.....	\$ 518.41
Cash received from dues for 1893.....	1,994.79
“ “ “ “ “ 1894.....	200.00
“ “ “ “ “ 1895.....	5.00
“ “ “ arrears of dues.....	105.15
“ “ “ subscriptions to JOURNAL.....	72.00
“ “ “ advertisements in JOURNAL.....	213.45
“ “ “ sales of back numbers.....	67.47
“ “ “ Initiation fee (F. J. Wulling).....	5.00
“ “ “ exchange.....	.07
	<hr/>
	3,181.34

##### EXPENDITURES.

General expenses.....	\$ 380.42
Journal of 1892.....	654.73
“ “ 1893.....	1,784.70
New York Local Section.....	115.00
Cincinnati Local Section.....	59.93
Providence “ “.....	18.33
Baltimore meeting.....	84.18
Overpayment of Dues returned.....	5.00
Initiation fee returned (F. J. Wulling).....	5.00
Balance on hand in bank of the Metropolis.....	74.05
Checks on hand.....	<hr/>

3,181.34

CHAS. F. MCKENNA, Treasurer.

No bills or claims, presented up to date and audited, remain unpaid. Accounts examined and found correct, E. and O. E.

FRANK T. KING, A. P. HALLOCK, DURAND WOODMAN.	} Finance Committee.
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New York, December 22, 1893.

Reports from the secretaries of the New York, Rhode Island, and Washington Sections were read, reporting a good attendance and the presentation of numerous papers at the meetings.

*The New York Section* has allied itself with other scientific bodies in New York City forming collectively the Scientific Alliance. There is no amalgamation in this nor does the council of the alliance to which each society delegates three members have any control over the internal affairs of the constituent societies. The present membership is 147 a gain of fifteen during the year. Total expenses for the year ending October 6, \$88.60. Present officers, Peter T. Austen, chairman; M. Loeb, secretary and treasurer; A. A. Breneman, Wm. McMurtrie, and A. C. Hale, executive committee; P. T. Austen, Wm. McMurtrie, and J. H. Stebbins, delegates to the Scientific Alliance.

*The Rhode Island Section* reports an addition of one name to its membership making a total of seventeen members. Nine meetings were held from September 1, 1892, to July 1, 1893, at which numerous papers of interest were presented. The officers are, John Howard Appleton, chairman; E. E. Calder, secretary-treasurer: and the chairman and secretary-treasurer, *ex-officio*, and Charles Catlin, executive committee.

*The Washington Section.* At the meeting of the Washington Chemical Society held May 11, 1893, the society voted to become a section of the American Chemical Society, and certain amendments to the constitution were presented to make it conform to such action. These amendments and a revised constitution were adopted December 14, which consummates the formation of the Local Section. No meetings were held between May 11, and October 31. The section has 94 members. The officers are F. P. Dewey, president; Cabell Whitehead and K. P. McElroy, vice presidents; E. A. de Schweinitz, treasurer; A. C. Peale, secretary; F. P. Dewey, T. M. Chatard, K. P. McElroy, E. A.

de Schweinitz, A. C. Peale, H. W. Wiley, F. W. Clark, Cabell Whitehead, and R. B. Warder, executive committee.

*The Cincinnati Section* presented no report. Since the meeting a report from the local secretary has been received which shows that the present membership is fifty-five a gain of seven. Eight meetings have been held at which numerous papers were read. The officers are: president, C. R. Stuntz; vice-presidents, W. Mumper and E. Twitchell; secretary, W. Simonson; treasurer, H. E. Newman; and directors, W. Dickore, J. U. Lloyd, A. C. Ramsay and E. C. Wallace.

The following papers were then read:

The Widespread Occurrence of Barium and Strontium in Silicate Rocks. *W. F. Hillebrand.*

The Estimation of Small Amounts of Barium and Strontium in Silicate Analysis. *W. F. Hillebrand.*

A Plea for Greater Completeness in Chemical Rock Analysis. *W. F. Hillebrand.*

A Study of the Distribution of the Oleo-resins in *Pinus Palustris*. *Oma Carr.*

Salicylic Acid in Food. *K. P. McElroy.* Read by title.

Utilization of Garbage. *Bruno Terne.* Read by title.

Adjourned at 2 P.M.

In the afternoon a visit was paid to the works of the Baltimore Copper Smelting and Rolling Company, under the guidance of members of the local committee. The raw material consists of Anaconda Matte which is worked up into copper by the ordinary method of roasting and smelting. The impure copper is then subjected to electrolysis and subsequently melted and cast. Another portion of the roasted copper oxide is boiled with sulphuric acid and the blue vitriol crystallized out and sold. Silver is separated by the addition of a small amount of common salt.

In the evening a dinner complimentary to the visitors was given by the local committee at the Eutaw House. Dr. Wm. Simon acted as toastmaster and H. W. Wiley, Wm. McMurtrie, Ira Remsen, F. W. Clarke, J. H. Appleton, Edward Hart, W. L. Dudley, and C. B. Dudley responded to toasts.

THURSDAY, DECEMBER 28.

Papers were read as follows:

Some Facts Relating to Type Writing Machine Oils. *Thomas Taylor.*

Report on the Determinations of Atomic Weights published during 1893. *F. W. Clarke.*

The Detection of Strychnine in an Exhumed Human Body. *W. A. Noyes.* Read by Edward Hart.

The Importance of the Study of Biochemistry. *E. A. de Schweinitz.* Read by C. E. Munroe.

Upon Uniformity in Sampling and Assaying Copper Bullion. *G. W. Lehmann.* Read by title.

The Preservation and Arrangement of Chemical Abstracts and Clippings. *Thomas M. Chatard.*

Historical Notes on the Electro-metallurgy of Zinc. *Charles Platt.*

The Phenylhydrazin Test for Glucose in Urine. *C. E. Pellew.* Read by title.

Expert Testimony. *W. P. Mason.*

The Boric Acid Springs of Tuscany. *W. P. Mason.*

Phosphorus in Steel. *C. B. Dudley.*

Some Points in the Volumetric Estimation of Phosphorus. *C. B. Dudley.*

Determination of Phosphorus by the Molybdate Method in Presence of Arsenic in Iron, Steel and Ores. *James O. Handy.* Read by C. B. Dudley.

The Analysis of Malt. *J. A. Miller.* Read by title.

Determination of Nickel in Steel. *Jos. Westesson.* Read by title.

Preliminary Note on Electrical Organic Analysis. *Edward Hart.*

Convenient Resistance Board for Use with Blackened Lamps. *Edward Hart.* Read by title.

After a recess of five minutes the secretary read a telegram of congratulation from A. B. Prescott, of Ann Arbor, Mich., as follows:

ANN ARBOR, MICH., December 26, 1893.

Prof. H. W. Wiley, or Secretary American Chemical Society,  
Baltimore, Md., (Hotel Rennert).

"I rejoice with Society upon the results of ninety-three; the membership enrolled, the JOURNAL established, the organization effected and the congress of chemists overflowing, each an event in American Chemistry; an event international is Bolton's Bibliography of Four-Hundred Years. With regret that I must be absent,"

ALBERT B. PRESCOTT.

The secretary was instructed to make a suitable response.

The report of the committee of canvassers was presented showing the election of H. W. Wiley as president; A. C. Hale, secretary; C. F. McKenna, treasurer; F. E. Dodge, librarian; C. F. Chandler, P. T. Austen, C. A. Doremus and H. C. Bol-



ton as directors to serve two years. C. B. Dudley, C. E. Munroe, Wm. McMurtrie and J. H. Appleton to serve as councillors for three years.

H. W. Wiley, chairman of the committee on new charter, reported that he had been unable to obtain a meeting of the committee, but that on his individual responsibility he reported in favor of the surrender of the New York Charter and the organization of the society under a new charter to be obtained from Congress. At the suggestion of Dr. McMurtrie and C. E. Munroe the matter was referred to the council for further examination with power to act.

On motion of Edward Hart the president was authorized to appoint a committee of seven to include the members of the committee on papers and publications to act as an advisory board on matters pertaining to the "style" to be used in the JOURNAL. (nomenclature, spelling, punctuation, etc.). The president subsequently named the following persons to act as members of this committee: Edward Hart, chairman; J. H. Long, Edgar F. Smith, A. B. Prescott, G. C. Caldwell, T. H. Norton and H. Carrington Bolton.

On motion of J. H. Appleton a committee of seven was appointed to petition Congress for a more specific wording of that part of the Tariff bill pertaining to importation of duty free apparatus and supplies for scientific work. The committee consists of C. E. Munroe, chairman; H. B. Nason, Edward Hart, E. F. Smith, J. H. Appleton, A. B. Prescott and W. L. Dudley.

Dr. Wiley thanked the society for the honor done him in a re-election to the office of president. He believed, however, as the office of president was entirely honorary that two terms for one person was a mistake. As the mistake had now been made he felt bound to accept, especially as a declination to serve would put the council to inconvenience and delay business that should be attended to promptly.

Mr. C. F. McKenna offered his resignation as treasurer, stating that he found the work required so much time that he felt unable to longer attend to it. Referred to the council.

On motion of F. W. Clarke the thanks of the society were voted to the local committee of arrangements, to President D. C.

Gilman and Prof. Ira Remsen, of Johns Hopkins University, for courtesies extended, to the Baltimore Copper Smelting and Rolling Co., the Lazaretto Chemical and Fertilizer Co., and the Maryland Steel Co., for the privilege of inspecting their plants, and to Baker, Whitely and Co., and the Rasin Fertilizer Co. for transportation.

Adjourned.

In the afternoon the members visited the works of the Maryland Steel Co., at Steelton. The tugs Sea-Wall and Chicago carrying the party down the bay.

These works comprise four large blast furnaces, two twenty ton Bessemer converters and a complete ship building plant. A recent addition is the immense shears operated by hydraulic power which were used in lifting Krupp's gun from the vessel to the car upon which it was transported to Chicago. The party were taken through the works by Mr. Frank T. King and through the Bessemer Steel department by Mr. G. F. Knapp.

*Local Committee of Arrangements.*—C. P. Van Gundy, chairman; W. B. D. Penniman, secretary; Wm. Simon, W. J. Gascoyne, R. D. Coale, Chas. Glaser, G. W. Lehmann, A. R. L. Dohme, A. J. Corning, Wm. Glenn and G. A. Liebig, Jr.

#### REGISTER OF MEMBERS IN ATTENDANCE:

Wm. McMurtrie,	W. F. Hillebrand,
Chas. F. McKenna,	G. L. Spencer,
P. Fireman,	H. B. Nason,
Walter B. Randall,	Wm. P. Mason,
Charles L. Parsons,	J. H. Appleton,
Chas B. Dudley,	E. C. Franklin,
E. W. Allen,	Thomas Taylor,
W. D. Bigelow,	G. A. Chalmot,
H. W. Wiley,	W. R. Orndorff,
Edward Hart,	A. P. Sharp,
W. J. Gascoyne,	Charles Platt,
W. B. D. Penniman,	R. M. Parks,
A. L. Browne,	Sam'l P. Sadtler,
W. Liman,	Thomas M. Chatard,
C. P. Van Gundy,	H. H. Hawling,
Wm. Bromwell,	G. B. Pfeiffer,
Wm. Simon,	G. F. Barker,
A. R. L. Sohme,	Geo. Steiger,
R. D. Coale,	Robt. B. Warder,

Chas. Glaser,  
Wm. Glenn,  
A. J. Corning,  
Charles E. Munroe,  
Eugene Byrnes,  
Wirt Tassin,  
August E. Knorr,  
Oma Carr,  
T. C. Trescott,  
Wm. H. Krug,  
F. W. Clarke,  
W. P. Cutter,

T. R. Wolf,  
H. B. Hodges,  
Edgar F. Smith,  
Wm. M. Groevsnor, Jr.,  
W. L. Dudley,  
G. W. Lehmann,  
J. B. Littlewood,  
W. N. Mumper,  
John Johns,  
Edgar Richards,  
Marcus Benjamin,  
Lyman B. Hall.

## THE WIDE-SPREAD OCCURRENCE OF BARIUM AND STRONTIUM IN SILICATE ROCKS.<sup>1</sup>

BY W. F. HILLEBRAND.

**A**MONG the mass of published analyses of igneous eruptive and metamorphosed eruptive rocks, those in which barium and strontium are noticed are few indeed, unless the work has been of a special nature, like that of Sandberger in the development of the lateral secretion theory. Yet the very numerous analyses of igneous eruptive rocks of all ages and kinds made in the laboratory of the United States Geological Survey during the past thirteen years, have shown that these elements are distributed widely and in considerable quantity, in the United States at least, and doubtless elsewhere.

The percentages of barium and strontium oxides when present are usually below 0.1 per cent. each, but higher amounts are by no means uncommon, and for certain districts seem to be the rule rather than the exception. Within the past year two series of rocks from Colorado and Montana have been analyzed, both of which are noteworthy for the high percentages of barium found in them. Of seven rocks constituting the Colorado series six held from 0.13 to 0.18 per cent. BaO, while in the seventh the percentage was 0.43. The SrO ranged from 0.07 to 0.13 per cent. for six, and was 0.28 per cent. for that one highest in BaO. Of thirteen geologically related rocks from Montana, embracing basic as well as acid and intermediate types, the range of BaO

<sup>1</sup> Read at the Baltimore meeting, December 27, 1893.

was from 0.19 to 0.37, with an average holding of 0.30 per cent. Three others of the same series contained 0.10 per cent. or less, while the seventeenth carried 0.76 per cent. BaO. The SrO ranged from 0.37 per cent. in the last instance to an average of 0.06 per cent. for the other sixteen.

In view of the above showing the question arises, why was not this general distribution sooner recognized? The answer is undoubtedly given by the statement that it has not been the custom among chemists to look for barium and strontium in analyses of the kind under discussion, and doubtless for the following reasons:

1st. A belief on the part of many that the two elements were absent from most rocks, this belief being based on the supposed rarity of the few rock-constituting minerals known to contain barium and strontium as noteworthy constituents.

2nd. Admitting the possibility of their presence in minute quantities, the unimportance as an aid to classification by the lithologist of the knowledge that a rock may contain a few hundredths of one per cent., more or less, of barium or strontium.

The unsoundness of the first argument has been sufficiently demonstrated by the data given above for rocks of the United States, which show likewise what serious errors may be incurred by neglect to test for the elements in question. Barium and strontium carrying minerals, sometimes with high percentages of one or both, are more common rock constituents than was formerly supposed.

With regard to the second point it may be said that if the present decade or the next may be unable to make use of the knowledge referred to, this will probably not hold true of the lithologists of a still later period—an argument perhaps equally applicable to other elements than barium and strontium.

Regarding a further reason why barium has undoubtedly often been overlooked, the reader is referred to the following paper.

## THE ESTIMATION OF SMALL AMOUNTS OF BARIUM AND STRONTIUM IN SILICATE ANALYSIS.<sup>1</sup>

BY W. F. HILLEBRAND.

**I**N testing qualitatively for barium and strontium in the course of analysis of natural silicates it has probably been the custom to rely upon the spectroscopic examination of the ignited calcium oxalate, on the assumption that, notwithstanding the well-known greater solubility of barium and strontium oxalates over the corresponding calcium salt, the latter would carry down enough of the former to render detection of barium and strontium by aid of the spectroscope a matter of no difficulty.

This assumption in the case of strontium is well founded as I have observed times without number, but it may be entirely fallacious in the case of barium. The twice precipitated calcium oxalate of the analyses marked "later" in the next following paper, afforded a very strong spectroscopic reaction for strontium, but failed to give one for barium, although the oxide of this element was a constituent of the rocks up to 0.76 per cent., and simply because the latter had been entirely kept in solution by the large amounts of ammonium chloride present. This observation suggested at once an explanation for the apparent rarity of barium in the silicate rocks of the earth's crust, and opened up a field for investigation as to the best course to pursue in the separation and estimation of the three alkaline earth metals under the conditions generally prevailing in rock analysis, that is to say, great excess of calcium over barium and strontium in presence of magnesium and large amounts of sodium and ammonium chlorides.

Brief consideration sufficed to reject recourse to collective precipitation of the alkaline earths by ammonium carbonate because of the well-known incompleteness of such precipitation under the prescribed conditions.

It seemed better to seek a separation of barium at the outset. This conclusion was fortified by the results of experiments undertaken to ascertain the behavior of strontium under conditions similar to and differing from the above. A large number of experiments were made with calcium, strontium, and barium sepa-

<sup>1</sup> Read at the Baltimore meeting, December 27, 1893.

rately, and then with mixtures of the former and either strontium or barium. The absolute amounts experimented with were kept low in order that the conditions usually obtaining in rock analysis might be as nearly as possible preserved. It was not for a moment expected that an exact method of separating considerable amounts of barium from either calcium or strontium would be discovered. The most that was hoped for was to work out a method suitable of application where relatively small amounts of strontium and barium occur with relatively large amounts of calcium. The outcome only in a measure fulfilled the hope raised by a few preliminary tests, but the results seem to be of sufficient interest to merit somewhat detailed description.

The precipitates were formed in ammoniacal solution at a boiling heat and were allowed to stand over night before filtering. They were washed but once or twice with cold water because of the very marked solubility of both strontium and barium oxalate in hot water, and even in cold water if the washing is prolonged. The filtrates were evaporated to dryness, ammoniacal salts were removed by heat, and after solution of the residue strontium and barium were precipitated as sulphates, the former after addition of alcohol. The sulphates were, when necessary, tested spectroscopically. The amounts of the different salts taken are purely arbitrary, except that the highest weights for BaO are the chemical equivalents of the highest for SrO.

## FIRST SERIES.

	Amount taken calculated as oxide.		(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> · H <sub>2</sub> O amount in excess of that required for conversion of total bases to oxalates. Grams.	NH <sub>4</sub> Cl Grams.	Total bulk of solution Cubic centimeters.	SrO in filtrate.	
	SrO	CaO				Weight.	Per cent.
1	0.0343		1	10	250	0.0080	23.3
2	0.0343		1	10	250	0.0045	13.1
3	0.0343		2	10	250	0.0032	9.3
4	0.0343	0.0560	1	10	250	0.0036	10.5
5	0.0343	0.0560	1½	10	250	0.00275	8.0
6	0.0343	0.0560	2½	10	250	0.0023	6.7
7	0.00384	0.0560	1	5	250	0.0003	7.8
8	0.00384	0.0560	1	10	250	0.0005	13.0
9	0.0010	0.0560	1	5	250	Faint sp'tro'pic trace.	
10	0.0010	0.0560	1	10	250	"	"

From the above it is plain (1-3) that, as was to be expected, strontium is incompletely precipitated by ammonium oxalate in slight excess and that its solubility is markedly lessened by increase of the precipitant. Furthermore (4-6), that calcium if present in quantity exercises a notable effect in promoting completeness of precipitation. Finally, that with very small amounts of strontium and a great excess of calcium the precipitation of the former is practically perfect in presence of a sufficient excess of ammonium oxalate, irrespective of considerable variations in the ammonium chloride. Additional experiments in which 5-6 grams of sodium chloride were added showed that this salt exercised a very slight but appreciable solvent effect on strontium oxalate. In entire absence of ammonium chloride on the other hand, precipitation of as much as 0.004 gram SrO is practically perfect in presence of 0.0560 CaO.

## SECOND SERIES.

	Amount taken calculated as oxide.		(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> · H <sub>2</sub> O, amount in excess of that required for conversion of total bases to oxalates. Grams.	NH <sub>4</sub> Cl Grams.	Total bulk of solution. Cubic centimeters.	BaO in filtrate.	
	BaO	CaO				Weight.	Per-centage.
11	0.0509		1	5	250	0.0230	45.2
12	0.0509		1	5	250	0.0089	17.5
13	0.0509		2	5	250	0.0070	13.7
14	0.0509		4	5	250	0.0051	10.0
15	0.0509		1	10	250	0.0457	89.8
16	0.0509		1	10	250	0.0243	47.7
17	0.0509		2	10	250	0.0138	27.1
18	0.0509	0.0560	1	5	250	0.0436	83.6
19	0.0509	0.0560	1	5	250	0.0293	57.5
20	0.0509	0.0560	1	10	250	0.0489	96.0
21	0.0509	0.0560	1	10	250	0.0458	90.0
22	0.0509	0.0560	1	10	250	0.0463	90.9
23	0.0509	0.0560	1	10	250	0.0346	68.0
24	0.0509	0.0560	1	10	250	0.0206	40.5
25	0.0135	0.0560	1	5	250	0.0109	86.7
26	0.0135	0.0560	1	10	250	0.0106	78.5
27	0.00906	0.0560	1	5	250	0.0074	81.7
28	0.00906	0.0560	1	10	250	0.0079	87.2
29	0.00226	0.0560	1	5	250	0.00177	78.3
30	0.00226	0.0560	1	10	250	0.00197	87.2

In this series (11-17) the same action of precipitant and ammonium chloride that was observed in the first series makes itself manifest, only in much greater degree. Numbers 18-24 show in general the marked effect of small variations in the

amount of precipitant, although an exception may be noted in 22 when compared with 21. Comparison of 19 and 22 with 11 and 15 respectively shows that the presence of calcium exerts no retentive effect whatever on the barium, in marked contrast with its behavior toward strontium. With decreasing amounts of barium, the calcium remaining constant as well as the excess of precipitant, the slight influence of large variations in the ammonium chloride is apparent from numbers 25-30. The general result is to show conclusively that considerable amounts of barium may be separated almost completely from calcium by a single precipitation with ammonium oxalate in presence of considerable ammonium chloride, provided the precipitant is used in slight excess only.<sup>1</sup> Additional tests have shown that sodium chloride, as with strontium, slightly facilitates the separation from calcium; also that a double precipitation will effect the quantitative separation of over two mgms. BaO from fifty-six mgms. CaO under the conditions of experiments 29 and 30. In cases like the last the whole of the BaO has been recovered from the filtrates and from the calcium as nitrate no trace of barium could be separated by ether-alcohol. It goes without saying that by increasing the ammonium chloride still larger amounts of barium may be equally well separated, as has been proven by numerous tests.

In endeavoring to apply the knowledge thus gained to the separation of barium from both calcium and strontium, which is the problem usually encountered in silicate rock analysis, difficulties at once suggest themselves, namely, those arising from the partial solubility of strontium oxalate in ammonium chloride, from the presence of five to ten grams of fixed alkali salts, whereby the exact recovery of barium and the strontium that may have gone into solution with it is rendered much less certain, and furthermore, from the increased solubility of the oxalates of the calcium group when, as is very often the case, magnesium is present in some quantity.

Of several experiments made to test the degree of accuracy attainable, first in absence of sodium chloride, then in presence

<sup>1</sup> This fact was first observed by the writer in 1884, and was mentioned in a foot note to p. 592, appendix B., of Mr. S. F. Emmons's Monograph on the Geology and Mining Industry of Leadville.



of that salt and also of one of magnesium, thus reproducing the unfavorable conditions usually encountered in actual practice, the following will serve as fair examples.

1.  $\text{CaO}$ , 0.0560;  $\text{BaO}$ , 0.0023;  $\text{SrO}$ , 0.00095;  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ,  $\text{H}_2\text{O}$ , one gram in excess,  $\text{NH}_4\text{Cl}$ , ten grams, total bulk of solution 250 cc. Two precipitations under precisely similar conditions. Found in filtrates, 0.00236  $\text{BaO}$ , showing but the merest trace of strontium. Recovered from the lime, 0.00085  $\text{SrO}$  holding fugitive spectroscopic traces of calcium and barium.

2. Precisely as in 1, with addition of  $5\frac{1}{2}$  grams  $\text{NaCl}$ . In filtrates 0.0023  $\text{BaO}$ , in lime 0.0006  $\text{SrO}$ .

3. As in 2 with addition of 0.09  $\text{MgO}$ . In filtrate 0.0023  $\text{BaO}$ , in lime 0.0006  $\text{SrO}$ .

It is apparent that the results are very satisfactory in 1, but that in 2 and 3 over thirty per cent. of the  $\text{SrO}$  has escaped detection although all the  $\text{BaO}$  was recovered. The amounts of both  $\text{BaO}$  and  $\text{SrO}$  taken in these tests exceed what is met with in the great majority of igneous eruptive rocks, and the error in  $\text{SrO}$  may therefore in most cases be disregarded, for after all an absolute error of twenty-five or even fifty per cent. in the estimation of a substance constituting only 0.1 per cent. of a rock is ordinarily of small moment compared with the ability to certify to its presence with approximate correctness.

The procedure for the separation of the alkaline earth metals in silicate rocks as followed by myself with a fair degree of success for some time past, I will now outline, expressly promising, however, that it is not suitable for universal application, but that it seems to be the only one to meet the requirements of ordinary silicate analysis with anything approaching accuracy.

After a double precipitation, which should be made in any case, the ignited oxalate precipitate will contain nearly all the strontia and none of the baryta if the latter does not exceed 0.2–0.3 per cent. of the rock. If a larger quantity than 0.3 per cent. is present the precipitation by ammonium oxalate must be repeated or the rest of the barium subsequently separated from the strontium by ammonium chromate. The strontium is separated from the calcium by extracting the thoroughly dry nitrates (150–160° C.) by ether-alcohol, which as clearly shown by the

recent exhaustive researches of Fresenius<sup>1</sup> is the only one of the older methods at all capable of yielding a fairly satisfactory result. Hereby of course, any barium that might have been retained is also removed. The strontium weighed as sulphate should always be tested spectroscopically for barium, the barium sulphate likewise for strontium, either salt being brought into condition for making the test by reducing for a very few moments the whole or a part of the precipitate on a platinum wire in the luminous tip of the Bunsen burner, and then moistening with hydrochloric acid. If a trace of barium should be found with the strontium the error is insignificant and may be balanced by the strontium remaining with the calcium nitrate.

Before destroying ammoniacal salts, either by ignition or by nitric acid, prior to estimation of magnesia, a few drops of sulphuric acid should be added to precipitate the barium<sup>2</sup> which otherwise might contaminate the magnesium pyrophosphate. I say *might*, for small amounts of barium, up to 3 or 4 mgms. of oxide, will pass into the filtrate from the ammonio-magnesium phosphate. Only in exceptional cases have I ever found a trace of barium in the pyrophosphate after accidentally or purposely neglecting to effect a prior separation by sulphuric acid.

As to the barium itself it is improper to accept the amount thus separated from the magnesia as representing the total amount in the rock or mineral. It will almost always be found lower than the truth, probably for the reason that there are so many opportunities during the analysis for slight losses in the form of sulphate. Barium is best estimated in a separate portion which may also serve with advantage for the determination of titanium. The powder is decomposed in a capacious crucible with hydrofluoric and sulphuric acids, evaporation being repeated twice at least to ensure removal of all quartz. After volatilization of the excess of sulphuric acid the dry residue is digested with water containing several cubic centimeters of sulphuric acid to surely retain all titanium in solution, and a

<sup>1</sup> *Ztschr. anal. Chem.*, 29, 30, 31, 1890, 1891, 1893. Separation by amyl alcohol as recommended by P. E. Browning, *Am. J. Sci.*, 43, 50, and 314, 1892, has not been tried.

<sup>2</sup> The barium sulphate thus formed is not separated by filtration till after destruction of the ammoniacal salts, and, if this has been effected by nitric acid, not until after evaporation to dryness.

few drops of hydrochloric acid, and the solution is allowed to settle for some hours. The ignited insoluble matter is evaporated with relatively much sulphuric and a little hydrofluoric acid till the latter is removed and a clear solution results, which is then poured into a few cubic centimeters of cold water. The precipitate will now be free from calcium in all probability, but may contain a little strontium from traces of which it is easily freed by repeating once or twice the solution in strong acid and reprecipitation by water.<sup>1</sup> Unchanged weight after the final precipitation is evidence of purity of the barium sulphate, and the spectroscope should confirm this. These last mentioned manipulations require little expenditure of time even when they have to be repeated, and the result is usually eminently satisfactory. If the first weight of the barium sulphate is but one or two mgms. it is rarely necessary to purify the salt further.

Such is the procedure when only small amounts of barium and strontium have to be estimated. Should they be present in amount exceeding, say, two mgms. for SrO, and four mgms. for BaO, or should with smaller contents a high degree of accuracy be desired, the already difficult analysis presents still greater difficulties. In such cases there remains no other way than to combine the barium and strontium found in the filtrates from the calcium oxalate with the strontium and barium separated from the oxalate itself, and to apply to the mixture the ammonium chromate method of separation as prescribed by Fresenius (*l. c.*). The practiced eye readily learns to judge by spectroscopic test of the ignited and weighed calcium oxide whether strontium is in sufficient quantity to necessitate this course, and the separate determination of barium as above described will decide with regard to that metal.

<sup>1</sup> If the rock happens to contain zircon this may, and probably will, remain with the barium sulphate until removed by appropriate means.

## A PLEA FOR GREATER COMPLETENESS IN CHEMICAL ROCK ANALYSIS.<sup>1</sup>

BY W. F. HILLEBRAND.

THE valuelessness to the mineralogist and geologist of many of the analyses of mineral substances made in earlier times is a fact too well-known to need substantiation. Defective methods of analysis, the difficulty of procuring pure reagents, and want of time for exhaustive examination have been largely responsible for this condition, but lack of appreciation of the fact, now so well established, that substances present in small amount may have an important bearing on the discussion of results, has no doubt contributed in no small measure to it.

Whatever the causes, the result has been the necessity for a vast amount of repetition in analytical work, and it behooves the present generation of chemists to heed well the warning and to work with a two-fold purpose in view, that of lightening the labors of those who come after us by enabling them to use our work with less supplementary examination, and of thereby enhancing our own reputations by meriting encomiums on work that has stood the test of time.

This monition applies to the lithologist as well as to the chemist, and the former should seek to make or have his analyses made as complete as possible, and not, as is so often the case, be content with determinations of silica, alumina, the oxides of iron, lime, magnesia, the alkalies, and water; even going so far sometimes as to ask the chemist to omit tests for other constituents that may be present in small quantity for the sake of getting a greater number of more or less incomplete analyses accomplished. The latter, it is true, may serve the immediate purpose for which they were intended, but their incompleteness may on the other hand not only conceal points fruitful of suggestion to the attentive mind, but, what is of still greater importance, they may be actually misleading. Enough instances of totally inaccurate conclusions to be drawn from them have fallen under my own observation to fully justify this plea in favor of greater completeness in rock and mineral analyses made for purely scientific purposes.

<sup>1</sup> Read at the Baltimore Meeting December 27, 1893.

This is shown by the difference between the following analyses. The specimens were taken and analyzed at widely separated times and by different persons, it is true, but they were unquestionably from the same rock mass in which, however much the relative proportions of the different mineral constituents might vary within certain limits, there can be no reason to doubt the general distribution of all the elements shown by the second analysis.

	Earlier Analysis	Later Analysis
SiO <sub>2</sub> .....	54.42	53.70
TiO <sub>2</sub> .....	....	1.92
Al <sub>2</sub> O <sub>3</sub> .....	13.37	11.16
Cr <sub>2</sub> O <sub>3</sub> .....	....	0.04
Fe <sub>2</sub> O <sub>3</sub> .....	0.61*	3.10*
FeO .....	3.52*	1.21*
MnO .....	....	0.04
CaO .....	4.38	3.46
SrO .....	....	0.19
BaO .....	....	0.62
MgO .....	6.37	6.44
K <sub>2</sub> O .....	10.73	11.16
Na <sub>2</sub> O .....	1.60	1.67
Li <sub>2</sub> O .....	trace	trace
H <sub>2</sub> O below 110°C.....	....	0.80
H <sub>2</sub> O above 110°C.....	2.76**	2.61
CO <sub>2</sub> .....	1.82	....
P <sub>2</sub> O <sub>5</sub> .....	....	1.75
SO <sub>3</sub> .....	....	0.06
F .....	....	0.44
Cl .....	....	0.03
	<hr/>	<hr/>
	99.58	100.40
Less O for F1.....		.19
		<hr/>
		100.21

Another instance of a similar kind is given below. Here again certain differences are explainable by natural variations

\* From the fact that repeated determinations of the iron oxides in this and related rocks from the same region show always a great preponderance of ferric oxide, it is not improbable that the figures given for the two oxides in the first analysis were accidentally transposed.

\*\* In the published analysis it does not appear whether this is total water, or, as seems probable, only that remaining above 100°C.

## 92 PLEA FOR GREATER COMPLETENESS IN ROCK ANALYSIS.

in the proportions of the constituent minerals, but it can hardly be doubted that  $\text{TiO}_2$ ,  $\text{BaO}$ ,  $\text{SrO}$ ,  $\text{P}_2\text{O}_5$ , and  $\text{SO}_3$ , were present in both specimens in approximately the same amounts. In the earlier analysis in this case determinations of some supposed unimportant constituents were purposely omitted or only made qualitatively, with results which cannot be otherwise than fatal to a full comprehension of the mineralogical nature of the rock.

	Earlier Analysis	Later Analysis
$\text{SiO}_2$ .....	44.31	44.65
$\text{TiO}_2$ .....	not est.	0.95
$\text{Al}_2\text{O}_3$ .....	17.20	13.87
$\text{Fe}_2\text{O}_3$ .....	4.64	6.06
$\text{FeO}$ .....	3.73	2.94
$\text{MnO}$ .....	0.10	0.17
$\text{CaO}$ .....	10.40	9.57
$\text{SrO}$ .....	....	0.37*
$\text{BaO}$ .....	....	0.76
$\text{MgO}$ .....	6.57	5.15
$\text{K}_2\text{O}$ .....	3.64	4.49
$\text{Na}_2\text{O}$ .....	4.45	5.67
$\text{Li}_2\text{O}$ .....	....	trace
$\text{H}_2\text{O}$ below $110^\circ\text{C}$ .....	0.77	0.95
$\text{H}_2\text{O}$ above $110^\circ\text{C}$ .....	....	2.10
$\text{H}_2\text{O}$ by ignition.....	3.30	....
$\text{CO}_2$ .....	....	0.11
$\text{P}_2\text{O}_5$ .....	....	1.50
$\text{Cl}$ .....	....	trace
$\text{SO}_3$ .....	....	0.61
	99.11	99.92

While strongly upholding the necessity for more thorough work, necessarily somewhat at the expense of quantity, it is far from my intention to demand that an amount of time altogether disproportionate to the immediate objects to be sought should be expended on every analysis. But I do maintain that in general the constituents which are likely to be present in sufficient amount to admit of determination in the weight of sample usually taken for analysis—say 1 gram for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , etc., to 2 grams for certain other constituents—should be sought for, qualitatively at least, in the ordinary course of quantitative

\* Not entirely free from  $\text{CaO}$ .

work, and their presence or absence noted among the results. If present in little more than traces that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0.02 or 0.06 per cent. In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present. Failure to do this may subject the analyst to unfavorable criticism when at some future time his work is reviewed and the omissions are discovered by new analyses.

Finally, whenever possible, a thorough microscopical examination of the rock in thin section should precede the chemical analysis. This may be of the greatest aid to the chemist in indicating the presence of unusual constituents or of more than customary amounts of certain constituents, whereby, possibly, necessary modifications in the analytical procedure may be employed without waste of time or labor.

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### ELECTROLYTIC SEPARATIONS.

By EDGAR F. SMITH.

Received December 16, 1893.

FREUDENBERG published an article recently entitled "Über die Bedeutung der elektromotorische Kraft für elektrolytische Metalltrennungen" (*Zeit. für phys. Chemie.*, **12**, 97), in which are facts of great importance to all interested in the determination and separation of metals in the electro-chemical way. Some statements, however, have been made by Freudenberg to which I feel it my duty to reply. I discover upon p. 116, for example, these lines: "Auch gelingt eine Trennung (Kupfer) von Kadmium, welche bisher nur bei Gegenwart von Salpetersäure möglich schien, vortrefflich, wenn man die Lösung mit 10-20 cc. verdünnter Schwefelsäure versetzt und mit einer Spannung von 2 Volt elektrolysiert. Das Kupfer wird rasch und völlig kadmium-freigefällt." This very separation was carried out successfully three years ago by Smith and Frankel (*Am. Chem. J.*, **12**, 104-112 and *Ber. d. Chem. Ges.*, **23**, Ref. 413) as will be observed from the literature references and the examples that follow:

1. To a solution containing 0.1975 gram copper and 0.1828 gram cadmium were added ten cc. of sulphuric acid (sp. gr. 1.09) and then 100 cc. of water. A current that liberated 0.3 cc. of electrolytic gas per minute acted upon the above mixture for twelve hours. The precipitated copper weighed 0.1968 gram.

2. A second experiment made under analogous conditions, except that the volume of sulphuric acid equaled fifteen cc. gave 0.1975 gram copper.

Freudenberg, while recognizing the fact that Smith and Frankel by electrolyzing solutions of metallic double cyanides effected many separations, seems not to be fully acquainted with all that has been achieved in this direction. Thus upon p. 113 he speaks of the separation of mercury from copper and alludes to the early statement of Smith and Frankel that if the quantity of copper exceeded twenty per cent. of the mercury the separation would not be satisfactory. This is true, but if Freudenberg had examined the literature that appeared later from this laboratory he would have found that Smith and McCauley (*J. Anal. Chem.*, **5**, 489 and *Ber. d. Chem. Ges.*, **24**, 2936) observed that "it is not only possible to separate these metals (mercury and copper) completely when present together in equal amounts, but even when the quantity of the copper is twice that of the mercury. In brief, the separation is as readily and accurately made as that of any other metal, *e. g.*, zinc from mercury. Furthermore, the presence of zinc, nickel, or other metals, in no wise, influences the separation of mercury from copper." I welcome, therefore, the results of Freudenberg's experiments with mercury and copper as confirmatory of those published by Smith and McCauley.

The observation of Freudenberg (p. 114) relative to the removal of gold when precipitated directly upon platinum will be found to be antedated by reference to *J. Anal. Chem.*, **5**, 204.

As to the criticism made upon p. 117, in reference to the separation of bismuth from copper in the presence of potassium cyanide and citric acid I would only add that Smith and Frankel made numerous separations of these two metals in this way. Their results were highly satisfactory. It is true that



they never used quantities of bismuth exceeding 0.1 gram. The dishes in which the decompositions were made were large and offered ample surface so that the bismuth deposit was in every case satisfactory.

The separation of copper from arsenic, in ammoniacal solution, as outlined on p. 118 of Freudenberg's article, has already been successfully made by McCay (*Chem. Zeitung*, 14, 509) and by Smith and Frankel (*Am. Chem. J.*, 12, 428).

Again upon p. 122 Herr Freudenberg confirms an early observation made by Smith and Frankel in reference to their inability to completely separate cadmium from nickel in cyanide solution, but he is apparently ignorant of a later series of experiments by these same chemists in which they give proof that cadmium and nickel in cyanide solution can be separated in the electrolytic way if caustic alkali be added to the solution undergoing electrolysis. An example will illustrate:

A solution, containing 0.1723 gram cadmium, 0.1600 gram nickel, 2 grams of caustic potash, 2.5 grams of potassium cyanide to which 150 cc. of water had been added, was electrolyzed with a current that gave 2.2 cc. of electrolytic gas per minute. The precipitated cadmium did not contain nickel; it weighed 0.1723 grams (*J. Anal. Chem.*, 6, 87, and *Ber. d. Chem. Ges.*, 25, 784).

Freudenberg correctly adds on p. 124 that "Die Cyanverbindungen \* \* \* \* \* haben jedoch unsere Trennungsmethoden bedeutend erweitert." This is evidenced by the many separations that have been effected in this laboratory in solutions of such compounds, *e. g.*

*Cadmium* from zinc, arsenic, tungsten, molybdenum, osmium, nickel, and cobalt; *gold* from palladium, platinum, copper, cobalt, zinc, and nickel; *mercury* from copper, zinc, nickel, cobalt, palladium, arsenic, tungsten, molybdenum, platinum, and osmium; and *silver* from copper, zinc, nickel, cobalt, arsenic, tungsten, molybdenum, platinum, and osmium.<sup>1</sup>

UNIVERSITY OF PENNSYLVANIA,

NOVEMBER 10, 1893.

<sup>1</sup> *Am. Chem. J.*, 11, 352, 264; 12, 428; 13, 417; *J. Franklin Inst.*, Dec., 1889; *J. Anal. Chem.*, 5, 489; 6, 87.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY,  
UNIVERSITY OF MICHIGAN.]

## DETERMINATION OF NICKEL IN NICKEL-STEEL.

BY E. D. CAMPBELL.

Received December 21, 1893.

THE growing importance of nickel-steel has rendered it desirable to have a rapid and accurate method for the determination of nickel in that metal, since the value of the steel is largely dependent upon the amount of nickel which it contains.

The methods in use at present for the determination of comparatively small amounts of nickel in the presence of a large amount of iron, and the separation of the nickel from the manganese and copper, with which it is in most cases associated in this steel, involves usually one or more basic acetate precipitations and the use of either hydrogen sulphide or of ammonium sulphide in the subsequent work.

On account of the strong tendency of the basic acetate of iron to retain nickel, and of the various objections to the use of hydrogen sulphide or of ammonium sulphide as a precipitant, it was thought desirable, if possible, to devise a method which should not be open to any of the above objections.

The following methods worked out with my assistance by Messrs. Richard Fischer and W. G. Wallace, will, I think, be found to be sufficiently accurate for technical work. As the result of a large number of experiments upon solutions of steel, to which had been added known amounts of nickel, manganese and copper, the last two being added in amounts varying from two to ten times that in which they would occur in nickel-steel, in order that any interference of these elements might be detected, it was found that the nickel could be accurately determined within 0.001 gram, the usual error not exceeding 0.0003 gram to 0.0005 gram. The amount of nickel recovered is usually a little higher than the true amount, the increase being due to the solubility of ammonium manganous phosphate, the manganese of which accompanies the nickel in the subse-

quent work. The principles involved in the processes below described are the following :

1st. The iron is precipitated as ferric phosphate in cold, strong acetic acid solution, under which conditions it precipitates perfectly free from nickel, although retaining a small amount of copper.

2nd. The copper is separated from manganese and nickel in hydrochloric acid solution by means of granulated lead.

3rd. The manganese and lead, which displaced the copper, are separated from the nickel by means of a cold ammoniacal solution of sodium phosphate.

4th. The nickel is determined in the ammoniacal filtrate from the phosphate of manganese and lead, by titration with standard potassium cyanide or by electrolytic deposition.

In case the nickel is accompanied by cobalt the latter metal remains with the nickel, and may be separated from it by any of the well-known methods after dissolving off the electrolytically deposited nickel.

The two methods described below are identical up to the point where a portion of the filtrate from the phosphates of manganese and lead is taken. The description of that part of the methods common to both will be first given, and then the two ways of treating the above filtrate for the final determination of nickel will be detailed.

#### DETAILS OF METHODS.

Take 2.2222 grams nickel-steel, place in a 500 cc. graduated flask, add twenty cc. nitric acid, sp. gr. 1.20, and five cc. strong hydrochloric acid sp. gr. 1.21. Boil until the solution is clear, which will usually require not more than from five to ten minutes. Remove from the plate and add 155 cc. sodium phosphate solution. If a slight precipitate should form which does not dissolve upon shaking, add carefully a few drops of hydrochloric acid until the solution clears up. Add twenty-five cc. strong acetic acid, sp. gr. 1.04 then 100 cc. sodium acetate solution, shake, dilute with water to 502.5 cc., shake again and allow to stand fifteen minutes. Filter through a dry, twenty-five cm. filter, catching the filtrate in a dry beaker. As soon as

enough of the filtrate has run through, which requires about ten minutes, draw off with a pipette 250 cc. of the filtrate, transferring to a number four beaker. This will give one-half of the solution, since it was found by experiment that the ferric phosphate from the amount of steel taken occupies 2.5 cc. Bring the solution to a boil and add twenty grams potassium hydroxide previously dissolved in forty cc. of water. Boil five minutes, then keep just below boiling point until the precipitate has settled and the solution is clear. This precipitates copper, manganese, and nickel so completely that the filtrate gives no color with hydrogen sulphide. Filter through asbestos, using a pump, decanting as much of the solution as possible before allowing the precipitate to get upon the filter. Wash with water. Dissolve the precipitate on the filter in a hot solution of six cc. strong hydrochloric acid with an equal volume of water. Wash the filter using only as much water as is necessary. To the solution in the flask, which should not exceed fifty cc. and should have a temperature of 40° to 50° C. add fifteen grams granulated lead and agitate at frequent intervals for five to ten minutes. This will completely precipitate the copper, a small amount of lead going into solution. Filter through a small glass wool filter, catching the filtrate in a number two beaker; wash the granulated lead with a small amount of water and boil the solution down until it does not exceed sixty cc. Add ten cc. of sodium phosphate solution, then ammonium hydroxide until a precipitate just forms, then hydrochloric acid until the solution just clears up, cool until cold, and transfer to a cylinder or flask graduated to 111.1 cc. Add five cc. strong ammonium hydroxide, sp. gr. 0.90, dilute to the mark, shake well and allow to stand fifteen minutes. Filter through a dry nine cm. filter, receiving the filtrate into a dry beaker. Draw off, by means of a pipette, 100 cc. of this filtrate which is equivalent to one gram of the original steel, and treat by one of the two following methods:

#### I. ELECTROLYTIC METHOD.

Transfer the 100 cc. of filtrate above mentioned to a large platinum dish having a capacity of about 200 cc. Add twenty-

five cc. of strong ammonium hydroxide, sp. gr. 0.90, and dilute to 175 cc. Electrolyze for at least four hours, preferably over night, using a current yielding four cc. of electrolytic gas per minute. This strength of current can be easily obtained by connecting three medium sized cells. A very satisfactory arrangement to avoid the excessive loss of ammonia and the spattering of the solution due to the active evolution of gas, is to cover the platinum dish with a large watch glass perforated in the center through which the positive electrode, consisting of a large platinum cone, is suspended by means of a platinum wire.

The end of the precipitation of the nickel is indicated when a drop of the solution placed upon a drop of ammonium sulphide gives no color due to nickel sulphide. When the nickel is completely precipitated, disconnect the battery, wash the nickel thoroughly with water, then finally twice with alcohol and, after draining off as much as possible, heat for a few minutes in an air-bath at  $110^{\circ}$  C. Cool and weigh. After getting the combined weights of the platinum dish and nickel, dissolve off the latter by warming with 5-6 cc. of nitric acid, sp. gr. 1.20, then wash the platinum dish by means of water and alcohol and dry and weigh as before. The difference in the two weighings gives the nickel.

It is more satisfactory to weigh the empty dish after the precipitated nickel has been dissolved off than before electrolysis, since in this way a shorter time will elapse between the two weighings and consequently less error will be introduced from variations in atmospheric conditions. This latter source of error may be still further reduced by employing as a counterpoise for the platinum dish, upon which the nickel is precipitated, a similar platinum dish washed, dried and cooled under the same circumstances as the former.

## 2. VOLUMETRIC METHOD.

Take 100 cc. of the filtrate from the phosphate of manganese and lead, add hydrochloric acid very carefully until the blue color of the double ammonium nickel chloride disappears, then add ammonium hydroxide, drop by drop, until the blue just reappears and add an excess not exceeding one cc. Dilute to 200

cc., add five cc. of cupric ferrocyanide indicator and run in standard potassium cyanide until the solution turns from the purple color of the indicator to a perfectly clear light straw yellow. Subtract from the number of cubic centimeters of potassium cyanide used the correction for the indicator. The difference gives the amount necessary to convert the nickel into the double cyanide of potassium and nickel. Multiplying this by the factor of the potassium cyanide, expressed in metallic nickel, gives the amount of nickel in one gram of the original sample.

#### SPECIAL APPARATUS AND REAGENTS.

500 cc. graduated flask with an additional mark at 502.5 cc.  
250 cc. drop pipette. 100 cc. drop pipette.

Glass stoppered cylinder or flask graduated to 111.1 cc. The graduated apparatus should be carefully calibrated and compared before using.

*Sodium phosphate solution*, made by dissolving 200 grams of the ordinary crystallized disodium hydrogen phosphate in 1860 cc. of water. Ten cc. of this solution contain one gram of the crystallized salt, and it requires seventy cc. to precipitate one gram of iron as ferric phosphate.

*Sodium acetate solution*, made by dissolving 250 grams crystallized sodium acetate in 820 cc. of water. 100 cc. of this solution contain twenty-five grams of sodium acetate, which is a slight excess over that which is necessary to convert the nitric and hydrochloric acids to sodium nitrate and chloride, with the liberation of the corresponding amount of acetic acid.

*Granulated lead* is of the same quality as that used in assaying. In size it should be that which passes through a sieve with twenty meshes to the inch, but remains upon a sieve with forty meshes.

Before using, the lead should be washed with dilute hydrochloric acid (one part acid to two parts water) in order to dissolve any oxide that may be present.

*Standard nickel solution*. This may be made from chemically pure nickel by dissolving 2.5 grams nickel in fifty cc. nitric acid, sp. gr. 1.20, adding an excess of hydrochloric acid, evaporating on a water-bath nearly to dryness, then diluting to 1000

cc., one cc. equals 0.0025 grams nickel. Or it may be made from chemically pure nickelous chloride by dissolving six grams in water with the addition of a few drops of hydrochloric acid, and diluting to 1000 cc. This latter solution must be standardized. In order to do this, take thirty cc., place in a large platinum dish, add twenty-five cc. of strong ammonium hydroxide, dilute to 175 cc. and electrolyze as in the electrolytic method for nickel.

*Standard potassium cyanide solution.* Take twelve grams of chemically pure potassium cyanide, dissolve in water, dilute to one liter. This must be standardized against a standard nickel solution. Since the presence of ammonium salts interferes somewhat in the titration with potassium cyanide, necessitating the use of a slightly greater amount of potassium cyanide than would be required if there were no ammonium salts present, it is better that the potassium cyanide be standardized under the same conditions as are met in analysis. To standardize the potassium cyanide, take 15–20 cc. of standard nickel solution, add six cc. of hydrochloric acid, sp. gr. 1.20, ten cc. sodium phosphate solution, ammonium hydroxide until the solution turns blue and then five cc. in excess. Now add hydrochloric acid until the blue color of the double nickel chloride disappears, then again ammonium hydroxide until the blue just reappears, and an excess not exceeding one cc. Dilute to 200 cc., add five cc. cupric ferrocyanide indicator, and run in potassium cyanide until the solution changes from the purplish color imparted by the indicator to a perfectly clear light straw yellow.

Divide the amount of nickel in the standard nickel solution taken by the number of cubic centimeters of potassium cyanide used, less the correction for the indicator. The result will give the strength of the potassium cyanide expressed in metallic nickel.

*Cupric ferrocyanide indicator.* Take 2.5 grams of crystallized cupric sulphate, dissolve in twenty-five cc. of water, add to this a solution of ammonium oxalate until the precipitate first formed just redissolves, then dilute to 500 cc. Dissolve 2.5 grams of potassium ferrocyanide in 500 cc of water, then slowly pour this solution into the cupric sulphate solution, stirring constantly

during the operation. This will give a deep purplish brown solution of cupric ferrocyanide which may precipitate partially on standing; but the precipitate so formed will be so fine that it will easily remain in suspension for a long time, upon shaking the bottle, thus insuring uniform composition. To find the correction for the indicator take 200 cc. of water, add 6-8 drops of ammonium hydroxide, then five cc. of indicator, taken after shaking the bottle well, and then run in potassium cyanide until the characteristic change of color is obtained.

Five cc. of cupric ferrocyanide of the above strength require from 0.15-0.2 cc. of potassium cyanide, one cc. of which is equivalent to 0.0025 of nickel. If a stronger end reaction is desired, ten cc. or even fifteen cc. of the indicator may be used and a suitable correction made.

Repeated analyses of steel have shown that the nickel may be determined, by the volumetric method, within from 0.0003 to 0.0005 gram of the true nickel content, duplicate determinations being made in three hours. The electrolytic method requires three hours to the time the solution is ready for electrolysis.

ANN ARBOR, MICHIGAN,  
DECEMBER 7, 1893.

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### PRELIMINARY REPORT OF THE COMMITTEE ON THE TARIFF.

THE COLUMBIAN UNIVERSITY,

WASHINGTON, D. C., January 15, 1894.

H. W. Wiley, Ph.D., Etc., Etc.,

President American Chemical Society,

SIR:—Your favor of January 5, 1894, announcing the appointment of the Committee on the Tariff, with the undersigned as Chairman has been received, and while from the nature of the case, it has not been possible to call the committee together for action, steps have been taken to secure information upon which to base our action.

We learn that efforts are being made to try and settle the question "What are philosophical or scientific instruments and prepa-



rations?" and in this particular we would call attention to the fact that in 1884 the Secretary of the Treasury referred this very question to the National Academy of Sciences, and that the Committee appointed by that body reported that an instrument is "philosophical," not in consequence of its special construction or function, but in consequence of the uses to which it is to be put, and that many instruments may be put both to uses which are philosophical and to uses which are purely industrial or commercial, it therefore appears to this committee that the terms "philosophical apparatus and instruments" should be held to cover all such instruments and apparatus imported for the purpose of improving natural knowledge. (*Rept. Nat. Acad. Sci.*, 66-67; 1885.)

From inquiry thus far of officials familiar with the operation of our tariff laws it appears that the difficulty in securing for educational institutions the full advantage of paragraph 667, page 47 of the Tariff of October 1st, 1891, arises from the fact that if dutiable articles used in commerce or the industries be admitted duty free for educational institutions the door is thrown open for the evasion of the law by those not entitled to the benefit of the Act.

It has been suggested by experts that this difficulty might be surmounted and that educational institutions might obtain that relief which Congress evidently intended they should have, by substituting for the present statute one providing that educational and other favored institutions be granted a rebate of duties on all dutiable goods and material consumed by them. In this case goods would be purchased directly from the "stock on hand" of dealers, or by advanced orders as heretofore, and when delivered the invoices would be accompanied by authenticated statements of the duties paid, which amounts would be returned on presentation of the statement to the Secretary of the Treasury or to his authorized agent. It is claimed that by this plan the delays now incident to purchase, and the difficulties arising from inconsistent appraisement will be remedied.

Your committee would respectfully ask that any who are interested in this matter should send their views and suggestions to the chairman of the committee and especially that they should

supply him with the particulars of any instances of failure of the act or inconsistencies in appraisement which may have come personally to their notice.

Respectfully substituted,

CHARLES E. MUNROE,  
Chairman.

## EXPERIMENTS ON THE ESTIMATION OF GRAPHITE IN PIG METAL.

BY FRANK L. CROBAUGH.

Received December 19, 1893.

THE determination of graphite in pig iron is often required. At furnace laboratories there is rarely time and equipment necessary to do this work by combustion. Appended are some details of experiments made in the search for a simple, yet accurate, method. In all cases counterpoised two 9 cm. filters were folded together and the filtration performed upon them. After partial unfolding and drying at a temperature not exceeding 100° C., (higher temperature chars paper after treatment) the excess of weight of the inner paper will be the weight of the graphite or graphite plus impurities. If now the paper containing graphite plus impurities (chiefly silica) be burned and the residual weight subtracted from the excess of weight of the inner paper, the difference may be graphite. Five grams of the same drillings were taken for each operation.

The metal contained 1.68 per cent. silicon. The washing in every instance was first with water and hydrochloric acid 1.1 sp. gr. until all iron was removed. The last washings were invariably with water. When there was intermediate treatment on the filter, it will be described with the experiment. In duplicate experiments, A and B, 125 cc. nitric acid, 1.135 sp. gr. was used as solvent and continued at gentle heat for one hour.

	A	B
Weight graphite plus silica.....	0.2105	0.2500
Weight of residual silica .....	0.0255	0.0658
	<u>5)0.1850</u>	<u>5)0.1842</u>
	3.70	3.68

The larger amount of silica in B is due to its standing at a gentle heat while A was being filtered. This strength nitric acid dissolves the most silicon according to Dr. Drown, but our experience has been that it separates on slight evaporation or on standing.

In duplicate experiments C and D, 60 cc. hydrochloric acid 1.1 sp. gr. was used as a solvent.

After complete solution 100 cc. of water was added to each and allowed to stand over night.

	C	D
Weight graphite plus silica .....	0.3500	0.3489
Weight of residual silica .....	0.1732	0.1721
	<u>5)0.1768</u>	<u>5)0.1768</u>
	3.53	3.53

The larger amount of silica separated rendered the burning of the graphite more difficult than in A and B. The amount of silica separated represents nearly all the silicon of the metal.

In experiment E, the solvent was 125 cc. nitric acid sp. gr. 1.135 added first, then immediately 12 cc. of Baker and Adamson's 40 per cent. hydrofluoric acid. Solution was perfect within five minutes at a gentle heat, after which the solution was boiled vigorously for five minutes longer, being constantly kept covered to prevent evaporation.

	E
Weight graphite plus silica .....	0.1768
Weight of residual silica .....	0.0000
	<u>5)0.1768</u>
	3.53

It was thought that hydrofluoric acid would either cause more of the silicon to go into solution and remain there or volatilize it from the boiling acid.

Some glaze was taken from the beaker but no severe corrosion occurred in several treatments in the same beaker.

Intermediate washing with a mixture, one-third strong ammonia and two-thirds water, was made with the hope of dissolving any silica that might still cling to the graphite.

On burning the filter containing the graphite nothing was left in the crucible but some minute dark spots, (likely traces of

elements seldom estimated in pig iron) too slight to effect the determination in question. In experiments A, B, C, and D, I feared that the silica weighed with the graphite might be hydrated and thus give too high results in graphite.

Experiment E provided means for eliminating this objection by wholly freeing from silica. Thus far no attention has been paid to the extraction of combined carbon from the graphite, except as far as the solvents used would do this work,, either by dissolving and retaining it, or evolving it. When the graphite of experiment E was washed with ammonia, after all iron was removed, brownish coloration appeared in the funnel tube during the first two washings, which suggested combined carbon in some form dissolved in ammonia. The following experiments were all started exactly the same as was E. The washing will be described along with results given.

	F	G
Weight graphite plus silica .....	0.1818	0.1800
Weight of residual silica .....	0.0000	0.0000
	<u>5)0.1818</u>	<u>5)0.1800</u>
	3.63	3.60

Both F and G were washed with alcohol, ether, and ammonia in order. Each of the three washings brought the brownish coloration as noted in E.

	H	I
Weight graphite plus silica .....	0.1820	0.1855
Weight of residual silica .....	0.0000	0.0025
	<u>5)0.1820</u>	<u>5)0.1830</u>
	3.65	3.66

H was washed with ammonia only. Copious brown color came. I was washed with alcohol and ether only. Brown color came.

	J	K	L
Weight graphite plus silica .....	0.1878	0.1830	0.1790
Weight of residual silica .....	0.0000	0.0000	0.0000
	<u>5)0.1878</u>	<u>5)0.1830</u>	<u>5)0.1790</u>
	3.75	3.66	3.58

J was also washed with alcohol and ether only. Brown color came. K was washed with alcohol, ether, and ammonia, in or-

der named as were F and G. It was observed that more color came with ammonia than with alcohol and ether. The alcohol-ether and ammonia filtrates of K were preserved and will receive attention later. L was washed with ammonia, alcohol, and ether in order. Scarce a trace of color came with alcohol and ether.

In none of these experiments except I was any residue left in the crucible except the dark spots previously alluded to, (soluble in boiling hydrochloric acid sp. gr. 1.20) and in that case, residual silica, showing that ammonia may be necessary to dissolve the last traces of silica, but not always necessary as proven by J.

From a comparison of results and character of washings, it is evident that ammonia is certainly as efficacious a wash as alcohol and ether for removing combined carbon or its compounds, and that where ammonia is used, alcohol and ether are unnecessary. The variation of the hydrofluoric acid results is not so great as to be inadmissible from a commercial stand-point.

This variation may be due to errors of manipulation, or to small graphitic crystals or nuggets crumbled rather than drilled from the pig and larger than the remainder of drillings thus rendering the sample of drillings not homogeneous.

These interlaced spongy particles of graphite, sometimes three mm. on a side are often noticed after solution of pig in 1.135 sp. gr. nitric acid. It may also be due to small amounts of fine graphite penetrating the inner paper and being retained by the outer paper or penetrating it also.

This phenomenon is sometimes noticed especially where retained by the second paper thus giving a dark color. Finally the chemical or mechanical action of the filtration may have disturbed the equality in weight of the two papers. Why then setting aside these sources of error and the dark spots on the crucible are we not weighing pure graphite, if the analysis be conducted as typified in experiment E? This *modus operandi* is shorter and free from the perplexities of the caustic potash method of Karsten. The alcohol-ether filtrate from K was evaporated to gentle dryness and formed a black mirror-like residue on the beaker, completely soluble in the ammonia wash

when warmed gently. The residue from the ammonia filtrate presented the same appearance but was not soluble in alcohol and ether, but readily taken up by ammonia.

Both filtrates on evaporation threw out the dissolved matter in brownish flocks. We hope to investigate this point more thoroughly and also the action of ammonia on the total carbon of pig iron as obtained by use of the double chlorides. Such work may aid in obtaining a better knowledge of the forms of combination of carbon with iron and the forms in which it is separated under different conditions.

Attention will also be paid to the character of spots on the crucible, but these would not be common to all pig iron and might exist to a greater extent in some than in others. I may note in conclusion that all filtrations were performed by aid of the pump, and that more closely concordant results might have been obtained had the filtrations been performed upon asbestos. It would also be interesting to determine whether the silicon of the metal under this treatment is volatilized or largely in solution.

LABORATORY OF STEWART IRON CO., L.T'D.,  
SHARON, PA., DECEMBER, 1893.

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## THE DETECTION OF STRYCHNINE IN AN EXHUMED HUMAN BODY.<sup>1</sup>

BY W. A. NOYES.

PROFESSOR T. G. Wormley in his book on the Micro-Chemistry of Poisons states that strychnine has never been found in an *exhumed* human body after a longer period of burial than forty-three days. His authority is the Ann. d' Hyg., April, 1881, 359. I have not been able to find in any chemical journal a contradiction of this statement, though there is a statement in the old edition of *Watt's Chemical Dictionary* which seems to be inconsistent with it. Under these circumstances the following account of a recent toxical case may be of some interest.

On April 26th of this year Drs. W. L. Athon and O. Mitchell, of Marshall, Ill., brought to me for examination the stomach, liver and a portion of the intestines of a child who died on June

<sup>1</sup> Read at the Baltimore Meeting, December 28, 1893.

23rd, 1892, and was buried the following day. The body was exhumed on April 25th, 1893, after a burial of 308 days. The material submitted for examination weighed 505 grams. About fifty grams were examined for arsenic and other mineral poisons with negative results. About 350 grams of the remainder were extracted with dilute sulphuric acid and alcohol by the usual methods. The aqueous residue which remained on concentration of the alcoholic solution contained a considerable amount of oily matter which was separated by filtration and washed as thoroughly as possible. This residue (A) is usually considered to be nearly free from alkaloids but it was further examined as described below.

The filtrate, after concentration, treatment again with alcohol, etc., was rendered alkaline with caustic soda and extracted with chloroform. The chloroform left, on evaporation, a considerable amount of oily bases which were partly volatile, as was shown by their fumes with hydrochloric acid. To separate the strychnine from this residue it was heated on a water-bath with a little concentrated sulphuric acid for two hours. After neutralizing the acid the solution was extracted with chloroform. The residue obtained, was treated again in the same manner, and that residue, again. Stoehr<sup>1</sup> has shown that when pure strychnine is heated to 100° with pure concentrated sulphuric acid, for some time, it is completely converted into the mono-sulphonic acid. Apparently in the presence of much foreign matter and with a small amount of acid in an open watch glass a considerable portion, at least, of the strychnine escapes this action of the acid. In any case, a portion of the last residue referred to above gave with potassium pyrochromate and sulphuric acid the violet color, changing after a short time to an onion red, which is characteristic of strychnine. While the use of concentrated sulphuric acid is open to objection and should never be resorted to when it is possible to avoid it, I do not know of any other method which would be successful in the case of such residues and such minute amounts of strychnine as were obtained in this case.

The oily residue (A) was treated with some purified ligroin,

<sup>1</sup> *Ber. d. chem. Ges.*, 18, 3429.

and very dilute sulphuric acid and the mixture was filtered with the aid of a pump in such a manner that both acid and ligroin were drawn through the filter. The acid solution and the ligroin were then separated and the strychnine was recovered from the solution and purified essentially as before. A considerably larger amount was obtained from this portion than from the first. The strychnine obtained was identified by the characteristic reaction with potassium pyrochromate and sulphuric acid, by the intensely bitter taste, by the crystalline form and double refraction as seen with the microscope, by the crystals obtained from the chloride with potassium chromate, and by the effect of about  $\frac{1}{10}$  of a milligram upon a frog weighing about two grams. The frog died from the effects of the poison, the symptoms of tetanus being fully developed within ten minutes after the dose was administered. The crystals of the chromate were chiefly of the branching forms; there was a little evidence of octahedra but they were not positively identified. The branching forms, however, developed the characteristic violet color when touched with concentrated sulphuric acid.

The total amount of strychnine recovered was estimated to be about two milligrams.

In the trial the chemical evidence was not contested. The defendant was, however, acquitted on other grounds.

ROSE POLYTECHNIC INSTITUTE,  
DECEMBER 23, 1893.

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## NOTES ON DETERMINATION OF NICKEL IN STEEL.<sup>1</sup>

BY JOSEPH WESTESSON, CHEMIST TO THE WASHINGTON NAVY YARD.

THE desirability of being able to determine nickel in steel by means of a shorter process than the one, now mostly in use, gave me cause some time ago, when a number of samples from nickel-steel plates were submitted for analysis to the ordnance laboratory, and when the tediousness of the said process became particularly apparent, to make some investigations in order to find a more direct method, and I shall beg permission to mention in a few words, what my trials led to.

In the process, above mentioned, the nickel is precipitated

<sup>1</sup> Read by title at the Baltimore meeting, December 28, 1893.



by means of hydrogen sulphide in the acetate solution, obtained by separating iron from nickel; the sulphide is filtered off, dried, ignited, dissolved in aqua regia and converted into the double sulphate with ammonia in order to obtain a suitable solution for electrolysis.

It occurred to me, that there ought to be some way, by which the nickel could be electrolytically precipitated *directly* in the acetate solution, and thus that part of the procedure, embracing the precipitation with hydrogen sulphide, entirely eliminated. If this could be done, it is evident, that there would be quite a saving of time, besides doing away with an unpleasant feature of the method. It became, therefore, my aim to simplify the old method in this peculiar part.

Now, as the presence of chlorides will prevent the electrolysis of nickel, and as the separation of the iron from nickel always had taken place in a chloride solution, I decided to bring my original solution into the shape of sulphates and then proceed on the old lines. After having made a number of more or less successful trials, I finally came to the conclusion, that the following method would answer the purpose very well:

One gram of the sample is dissolved in twenty cc. of sulphuric acid of 1.16 sp. gr., and the solution kept boiling for some time, whereupon five cc. of weak nitric acid is added in small portions. The solution is now evaporated until all the nitric acid is expelled, allowed to cool, water added and heated until clear. Neutralization with carbonate of soda is done in the usual way, but care should be taken not to carry it too close to the point of neutralization. Add water so as to make the bulk 375-400 cc. and precipitate with acetate of soda; filter into a casserole and evaporate the filtrate over a moderate flame; redissolve the ferric precipitate and repeat the precipitation twice, taking care not to make the bulk more than 400 cc. each time, and adding each filtrate to the first one. When the filtrates have been evaporated down to 400 cc., add ten cc. of concentrated ammonia and boil for a few minutes. The manganese will then settle out, evidently as  $H_2O, MnO$ , and is filtered off, whereupon the filtrate is ready for electrolysis. If the ammonia should be added to the concentrated filtrates, when *cold*, the manganese

will not separate out but will interfere considerably with the electrolysis later; it will in that case not only settle out at the anode, but will in fact contaminate the nickel on the cathode, not as loosely settled dioxide but alloyed with the nickel. When, on the other hand, the manganese is precipitated by ammonia in the hot solution, the nickel is to a small extent carried along with the manganese, but I have in all my experiments never found the nickel, lost in that way, amount to more than one to one and a half per cent. of the amount of nickel present in the steel.

How this modification of the old process compares with the original a few results will show.

In a nickel-steel, containing 3.50 per cent. nickel, determined by the old process, the amount found by the modified process in five different analyses was: 3.42 per cent.—3.51 per cent.—3.48 per cent.—3.51 per cent.—3.43 per cent., and in another steel containing 0.19 per cent., the following amounts were found: 0.18 per cent.—0.19 per cent.—0.19 per cent.

The time necessary for analysis of this kind I have found to be about eight hours. Thus, if the analysis is commenced at 8 A.M. the solution will be ready for electrolysis at twelve o'clock, or before; with seven or eight Grove cells in good condition the analysis should be concluded at 4 P.M. I have invariably commenced at noon and left my cylinder over night on four Grove cells, the separation of iron from nickel being completed about four o'clock, or sometimes a little later.

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### A CORRECTION.

BY H. L. PAYNE.

Received January 29, 1894.

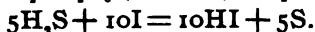
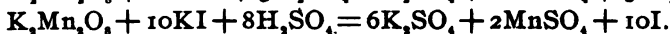
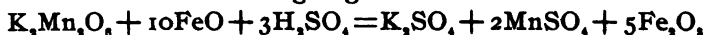
IN the *Journal of Analytical and Applied Chemistry* for September, 1892, 6, No. 9, I published 'A Method for the Preparation of a Standard Iodine Solution,' and on page 482 I have taken the molecular weight of two atoms of iron as 128 instead of 112. This singular error which vitiates the entire calculation following it, has been called to my attention by several readers and I desire to correct the mistake and again call attention to the method itself. If any one has been unfortunate

enough to take the figures just as I gave them, he has no doubt been disappointed with the method. To such I make a humble apology and ask that they try again using the following changes.

The relation between the iron and the sulphur value of a permanganate solution is 112 to 32 or 7 to 2 instead of 8 to 2 and of a phosphorus permanganate solution with an iron value 6,141,285 cc. should be taken to make one liter of iodine solution titrating 0.01 per cent. S on five grams iron, instead of 325.7 cc.

To make the whole matter clearer I may state the process of computation in a more general form making use of the atomic weights 56.00 for Fe and 32.06 for S. To make an iodine solution titrating exactly 0.0001 grams S per cc.—0.01 per cent. S per cc. on one gram of substance taken—divide 349.34 by the iron value, *i. e.*, the grams per liter or milligrams per cc., of the permanganate solution to be used. This gives the number of centimeters of such a solution to be used in making one liter of iodine solution. If more than one gram of substance is taken, multiply the number accordingly: thus for a permanganate solution whose iron value is 0.005 grams Fe per cc., take 69.87 cc. to one liter, or if five grams of iron or steel be used in the sulphur determination, take 349.34 cc. per liter.

The reactions in the foregoing method are as follows:



therefore  $\text{K}_2\text{Mn}_2\text{O}_8 = 10\text{Fe} = 10\text{I}_2 = 5\text{S}_8$ ,

or  $2\text{Fe} = \text{S}_8$ .

I hope now that this method has been correctly presented to the readers of THE AMERICAN CHEMICAL JOURNAL, that it will be made of the service which I believe its simplicity and accuracy deserves. I have tried it for over three years and have never had the slightest trouble.

CITY LABORATORY,  
CLEVELAND, OHIO.

## A RAPID AND ACCURATE METHOD OF DETERMINING THE MOISTURE AND OIL IN LINSEED CAKES AND OTHER FEEDING STUFFS.<sup>1</sup>

BY A. P. AITKEN, D. SC., CHEMIST TO THE HIGHLAND AND AGRICULTURAL SOCIETY OF  
SCOTLAND.

**I**T frequently happens that when the same sample of linseed cake is analyzed by different chemists very considerable differences occur in the proportions of oil and moisture found by them.

The explanation of these discrepancies is to be found, not only in the different methods employed, but also in the inconstancy of the results obtained by the same method.

*Determination of Moisture.*—As regards the determination of moisture, the common practice in this country is to expose one or two grams of a finely ground sample in a water-bath for two hours and to regard the loss of weight as the measure of the moisture. A recent examination of this method has shown me that it may be very inaccurate and that uniform results cannot be obtained by it.

The amount of heating which a sample gets in an ordinary water-bath during two hours may not be sufficient to deprive it of all its moisture. The temperature within the bath is not constant and it is always below 100° C. The temperature of the external air, the amount of ventilation, the frequency with which the door is opened, the quantity of the sample used, the nature of the vessel containing it whereby a greater or less amount of surface is exposed to the current of hot air, are all fluctuating conditions. Moreover, in the case of linseed cake, the sample continues to absorb oxygen during the whole time of its exposure in the bath and it does so the more rapidly the higher the temperature and the greater the surface exposed.

It thus happens that when a sample of finely ground linseed cake is exposed in a water-bath it goes on losing weight from loss of moisture for a time and thereafter gains weight from ab-

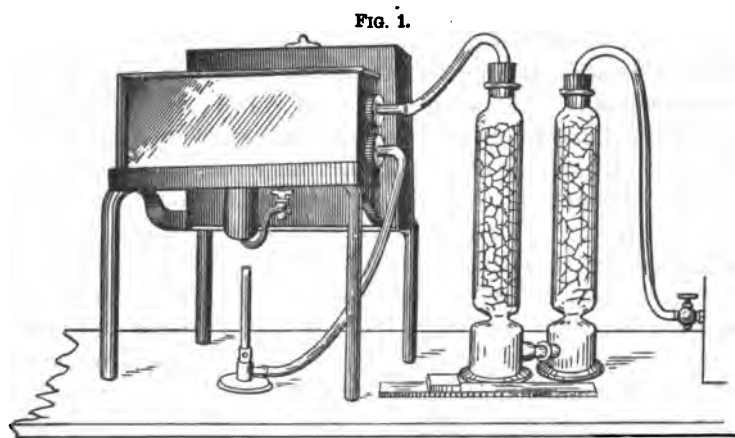
<sup>1</sup> Read before the World's Congress of Chemists, August 22, 1893.

sorption of oxygen. Therefore, the time at which the sample ceases to lose weight is not that at which the sample is dry but only the time at which the loss of moisture and the gain of oxygen counterbalance each other.

In order that the sample may be thoroughly dried and that it may at the same time suffer no oxidation, it must be dried in an atmosphere from which air is excluded. An atmosphere of hydrogen is excellent for the purpose, but one of coal gas does quite as well and it is most readily obtainable. I have used coal gas for the purpose for some years and it is used also in some of the continental laboratories.

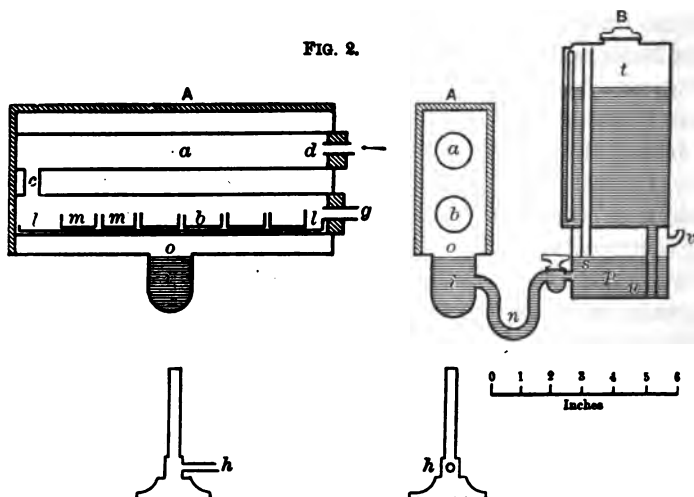
The apparatus I am about to describe secures that the sample is dried exactly at the temperature of boiling water and is so constructed that the coal gas is heated to that temperature before it comes in contact with the sample. It may be made of any dimensions, but the size which I prefer is that described below and capable of drying eight samples in an hour and a half.

The apparatus consists of a small rectangular box, ten inches long, four inches deep, and two inches wide, placed on edge as shown in Fig. 1, and in sections longitudinally and transversely, Fig. 2, A.



Through the box from end to end pass two hollow cylinders made of telescope tubing, and soldered into the box at each end.

The box is simply a steam-bath to heat the two tubular chambers, which are fitted at one end with the perforated corks and have the other end either closed with corks or entirely soldered up as in the diagram. The upper tubular chamber *a* is for heating the gas, and the lower one *b* for drying the samples, which are contained in little aluminum boats *m m* resting on a carrier of brass *l l* which slides into the chamber.



These boats, capable of holding one or two grams of cake, weigh only about one to two grams each, and are, therefore, very well adapted for weighing small quantities. The gas from the tap is led first through two drying bottles, filled, one with soda-lime and one with chloride of calcium, and enters the apparatus by the tube *d* in a perfectly dry state. It passes along the upper chamber *a*, where it is heated, and then through *c*, which is a tube connecting the upper and lower chambers. It arrives at the lower chamber *b* both hot and dry and passes along, drying on its way the samples (usually one gram each) contained in the little aluminum boats *m m*, eight of which can be accommodated on the carrier. The gas leaves the apparatus by *g*, and may be burnt there, but as the flow of gas is sufficient to keep a small Bunsen going, I connect the tube *g* with the Bunsen *h*.

The flame of this little Bunsen keeps the water in the thimble-

shaped cup *i* briskly boiling. The water in the thimble (about 1-2 ounces) is kept constantly at the level *o* by its connection with the automatic cistern B connected with the bath by the tube *u*, which is bent downwards and up again so as to prevent hot water from passing back into the lower section of the cistern *p*. As soon as the level of the water in this lower section falls below the mouth of the tube *s*, a bubble of air passes up the tube into the upper cistern *t*, and a corresponding quantity of water flows into the lower section through *u*, and restores the level of the water. A small hole *v*, into which an upwards bent tube is fitted, allows air to enter the lower section. The object of the upturned tube is to prevent water from spilling out of the air-hole, when the apparatus is carried about. This cistern contains more than a day's supply of water, and gives no trouble, and is supported along with the bath, on a light iron frame, as shown in Fig. 1. The inside of the bath is thus constantly full of steam, which escapes by a hole at the top about  $\frac{3}{16}$  of an inch in diameter. The bath is made of copper, but its entire surface is protected against contact with the surrounding air by means of asbestos sheeting  $\frac{1}{8}$  inch thick.

The temperature in the upper chamber is thus kept constantly at the boiling-point of water, and not several degrees below it, as is usually the case in even the best water-baths. By means of this small apparatus, eight one-gram samples of cake can be dried within two hours. They are removed by drawing out the carrier, transferred to an exsiccator, and weighed in the aluminum trays, whose weights are known and deducted, thus giving the moisture. The results are perfectly accurate, and the cost in gas is very small—only about one cubic foot per hour.

The samples are now ready to have their oil extracted and estimated.

It is not essential that the last traces of moisture should be removed before the oil is extracted. If the sample is dried for half the time required to completely dry it, it is in a suitable condition for oil extraction. Nine-tenths of the moisture will have gone by that time, and the presence of about one per cent. of moisture does not appreciably affect the amount of oil extracted.

I prefer to take the samples whose moisture I have estimated, and which are completely dry, because I have a method of extracting oil by which even very small quantities of oil can be accurately estimated, and which possesses the further advantage of being more rapid than any other method that I know of.

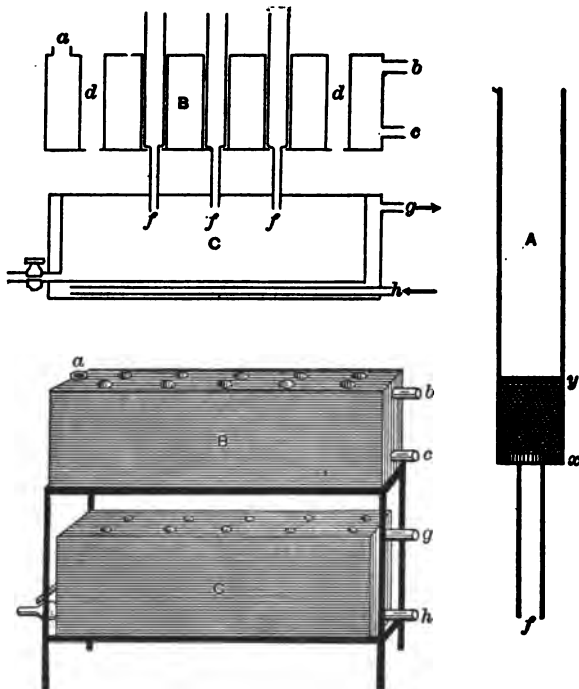
*Solvent for Oil in Cakes.*—Ether, bisulphide of carbon, or benzene, are the solvents usually employed, but as ether is the one which is most common, most rapid, and most comfortable to work with, I prefer it to the others. It is a little more expensive, but the quantity used in oil determinations is small; the additional cost is more than compensated by the advantages mentioned. Ordinary pure ether, as supplied by wholesale chemists, having a specific gravity of 0.73, is sufficiently pure and dry for the purpose of oil extraction; but as most of the ether used is recovered by redistillation in the laboratory and may contain water, it must be dried before being again used. This is sufficiently accomplished by shaking it up with chloride of calcium repeatedly for some days, and redistilling.

*Determination of Oil.*—The oil may be determined either by directly weighing the oil extracted, or by weighing the dried substance before and after the oil is extracted, and determining the oil by the difference of the two weighings. There are two objections to the former method. In the first place, the flask in which the oil is caught is itself very heavy and presents too great a surface; and in the second place, the evaporation of the residual ether in the drying chamber takes a long time, and the surface of the oil becomes covered with a thin pellicle due to oxidation. The latter method is much to be preferred if a suitable apparatus can be had for doing the work simply and rapidly. The apparatus I have devised for that purpose is very simple, and is shown in Fig. 3. It consists of a set of brass tubes, polished smooth inside, see Fig. 3, A, which is half the actual size, and is represented as charged with the dried sample. In charging the tube, the first thing required is to drop into it a small disk of wire gauze *x*, and then to insert a single or double wad of filter-paper, which is cut to fit the tube tightly, and pushed home with a ramrod. (I use a cork borer of the proper size for cutting the wads, and a piece of glass rod flattened out at the end



while hot as a ramrod.) The object of the wire gauze disk is to facilitate the flow of the ether through very fine powders, such

FIG. 3.



as ground grain, and also to enable the sample to be removed from the tube more easily after the oil is extracted. In the case of oil cakes the wire gauze disk may be dispensed with.

The sample is then poured in through a little metal funnel whose neck just fits the extraction tube. Any powder adhering to the funnel is brushed in with a camel-hair brush, then another wad *y* is patted in on the top of the sample, carrying with it any powder that might have adhered to the side of the tube and leaving the upper part of the tube clean and bright. The tube is now put into one of the holes in box *B*, which is simply a warming box made of zinc, shown also in section.

The holes *d d*, etc., are tubes which pass through the box from top to bottom, and are made a shade wider than the ex-

traction tubes, which should drop in easily. As soon as the extraction tubes are filled they are dropped into these tubular openings, which are provided with a ledge at the base to sustain the extraction tubes.

Hot water is poured into the box at *a*, or a constant current of hot water may be made to flow through the box, entering at *b* and flowing out at *c*, by attaching these by means of tubes to a copper coil under which a Bunsen is burning at a safe distance. At first I used the circulation method, but now I prefer to have no gas burning anywhere near the extractor. It is quite convenient to supply hot water at *a*, and withdraw the cooled water at *c* from time to time. As soon as the extractor tubes are dropped into their places, ether is poured into them to within an inch of the top, and by the time that the five tubes are thus filled the ether will be boiling in the first tube. A cork is now firmly fixed into each tube in succession, thus preventing the ether-vapor from escaping, and the presence of the confined vapor forces the boiling ether down through the samples and out through the lower openings *f* into little bottles placed beneath, so that the oil may be collected from each tube separately. If the oil of each tube is not to be kept separate, the mouths of the extractor tubes are made to dip into a zinc box *C* beneath, through small holes on the top, and there the oily ether collects and is run off from time to time, and redistilled for future use. There is considerable loss of ether by this method, but that is much reduced as one becomes expert in handling the apparatus; and if the other box below is provided with double walls between which a current of cold water is kept flowing through the openings *g*, *h*, the loss from evaporation is still further reduced.

This process of filling the tubes with ether is repeated ten, fifteen, or even twenty times, according to the difficulty of extracting the oil. The operation is complete when a drop or two of ether, falling from the exit *f* towards the end of an extraction, is caught on a clean watch-glass and evaporated without leaving any residue. The extractor I use in my laboratory is fitted for ten tubes, and after a little practice the oil from the ten samples of cake can be extracted with it in one hour. The extraction of oil from a sample, by means of Soxhlet's apparatus, which is the

one chiefly used at present, takes about five hours, so that this little apparatus has a great advantage over it as regards speed; but many comparative tests have proved that it also has the merit of making a more thorough extraction of oil. This is due to the fact that the extraction is made with boiling ether, and that no oily ether that has once been washed through is able to run back upon the sample again, as is the case with Soxhlet's apparatus. In extracting the oil from some substances, such as grain or other starchy powders, the resistance to the passage of ether is so great that even a tightly-fitting cork is apt to be blown out by the pressure of the vapor. In such cases I use caps with a cork washer inside, which fit on to the top of the tubes with a screw of half a turn which is very rapidly adjusted.

When the oil has been completely extracted, the removal of the sample is a neat and easy operation. It is done by inserting the cut end of the glass ramrod into the opening *f* and slowly pushing out the sample (wads and all) into a weighed aluminum capsule. The wads are now removed, after brushing off any particles of powder adhering to them with a camel-hair brush, and the dry powder, after exposure for a short time to a temperature of 100° C., is cooled in an exsiccator and weighed. The difference between that and the former weighing is the weight of the oil extracted.

It is evident that the accuracy of the oil determination by this method depends upon the accuracy of the determination of the moisture; but as by the method above described the moisture can be accurately determined, there is no danger, if that method is adopted, of making any error in the estimation of the oil. In estimating moisture in the ordinary way it is considerably underestimated, usually to the extent of one-twentieth or more, and in such circumstances that which is underestimated in the moisture is usually added to the oil; for the common practice is to determine the percentage of moisture in one part of the sample, the percentage of moisture and the oil together in another, and to subtract the former from the latter, so as to give the percentage of the oil.

It thus happens that in the analysis of an ordinary linseed

cake differences of two or even three per cent. are not unusual in the percentage of oil found by different analysts.

I have submitted this method to a long series of tests in my laboratory during the past winter and I have been so satisfied with the accuracy and uniformity of the results obtained by it and with the simplicity and rapidity of the whole process that I cordially recommend it to agricultural chemists in America and especially to those who have small laboratories and a large number of samples to analyze.

The apparatus is not costly and I hope the description I have given of it is sufficiently clear to enable it to be easily understood and imitated.

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## ON THE DETERMINATION OF NITRATES IN POTABLE WATER.

BY AUGUSTUS H. GILL.

Received January 16, 1894.

### PART I.

THE remark of Tiemann,<sup>1</sup> that the estimation of no other substance has so constantly occupied the attention of the analytical chemists of the last decade, to the extent to which the determination of nitric acid has engaged (literally "enchained") them, will, I think, be appreciated by all those who have worked upon the subject. Perhaps no determination requires more care, or occasions more trouble in its execution, or is more unsatisfactory when finished, than the one in question.

There are two general modes of procedure:

- a. The direct estimation, and
- b. The reduction to ammonia.

#### a. DIRECT ESTIMATION.

The direct processes which have been found to give the best results are those of Schulz-Tiemann,<sup>2</sup> Schloesing-Reichardt,<sup>3</sup> Crum-Lunge,<sup>4</sup> and Marx-Trommsdorf.<sup>5</sup> These are only appli-

<sup>1</sup> Tiemann Gaertner "Wasseranalyse" 3rd. Ed'n., p. 168.

<sup>2</sup> *Ber. d. chem. Ges.*, 6, 1041.

<sup>3</sup> *Ztschr. anal. Chem.*, 9, 24.

<sup>4</sup> *Phil. Mag.*, (3), 30, 426.

<sup>5</sup> *Ztschr. anal. Chem.*, 9, 171.

cable where relatively large amounts of nitrate are to be estimated, over 0.6 parts of nitrogen as nitrate per 100,000, and even with this quantity two or three hundred cc. of the water must be evaporated for use. This concentration is objectionable as it offers an opportunity for the oxidation of nitrites and their decomposition with loss of nitrogen,<sup>1</sup> and also for the oxidation of organic matter, and where many determinations are to be made it is very troublesome.

There is too, a decided advantage in estimating the nitrogen contents *immediately upon receipt of the sample, and if possible, upon the water as received.* This has been pointed out by Tidy<sup>2</sup> in reference to the carbon contents of a water, and applies with still greater force to the nitrogen which is more susceptible to change.

Another direct method is the phenolsulphonic acid process; it originated with Sprengel<sup>3</sup> and apparently fell into disuse until it was again brought to notice by Grandval and Lajoux.<sup>4</sup> Since then articles upon it have appeared by Fox,<sup>5</sup> Johnson,<sup>6</sup> Lindo,<sup>7</sup> Smith,<sup>8</sup> Bartram,<sup>9</sup> and Hazen and Clark.<sup>10</sup>

The two latter have criticised the process severely, and it seems to me unfairly, and it was with the idea of seeing how far

<sup>1</sup>  $\text{NH}_4\text{NO}_3 = 2\text{H}_2\text{O} + \text{N}_2$ .

<sup>2</sup> *J. Chem. Soc.*, 35, 53 and 97.

<sup>3</sup> *Pogg. Ann.*, 121, 188.

<sup>4</sup> *Compt. rend.*, 101, 62.

<sup>5</sup> *Tech. Quarterly*, 1, 1.

<sup>6</sup> *Chem. News*, 61, 15.

<sup>7</sup> *Chem. News*, 58, 1, 15, 28.

<sup>8</sup> *Analyst*, 10, 197.

<sup>9</sup> Bartram, *Jour. Frank. Inst.*, March 17, 1891, has published an article entitled "A Source of Error in the Determination of nitrates in Water by the Phenolsulphonic Acid Process," in which he says it was found that the phenolsulphonic acid undergoes a change after preparation. As ordinarily prepared, it may possibly undergo a change to the para acid; any difficulty is now obviated by the use of the pure disulphonic acid. I think the method has been submitted to an unusually severe test, 0.5 parts of nitrogen to 20 parts chlorine being very rarely met with in water analysis. It is inadvisable to estimate nitrates higher than 0.1 as it cannot be done with accuracy. Possibly the nitrate solution itself may have varied. I have solutions which contained 1 part of nitrogen as nitrates per 100,000 and which in the course of seventy-two hours showed but 0.04 part, and in ninety-six hours none whatever. Another containing 4.5 parts, showed at the end of six days but 0.25 part.

<sup>10</sup> *J. Anal. Appl. Chem.*, 5, 1.

their critique could be supported by experiment that this investigation was undertaken.

The process consists in evaporating the water,—usually ten cc.,—to dryness in a porcelain dish, treating the residue with phenolsulphonic acid, diluting with water and neutralizing with ammonia. In presence of nitrates, ammonium picrate is formed, the color of which is matched by standard solutions of potassium nitrate which have been treated in like manner.

One of the principal objections is the formation of the three nitrophenols "the principal products being the ortho and para *mono* nitrophenol." This cannot be the case: according to Richter,<sup>1</sup> in the presence of a large excess of strong sulphuric acid—as we have here—the nitration goes farther, forming the di and tri-substituted compound. Granted, however, that the different amounts of these compounds were formed, it would be exceedingly anomalous to have under exactly the same conditions, at one time a large quantity of dinitrophenol formed, and at another time a large quantity of the trinitro body. Furthermore, the readings given in their comparative table of the various nitrophenols are probably incorrect; it has been found impossible to read colors as deep as 1.2 parts nitrogen per 100,000 in an eight inch tube more closely than twenty-five per cent.

The suggestion of one of them,<sup>2</sup> of making up standards in eight inch tubes and allowing them to stand "for months," has been found to be of no advantage, as a very decided deterioration does take place. The other suggestion, of making up standards by dilution of a solution obtained by treating a large quantity of potassium nitrate, is open to the objection that the colors produced are not the same as those from making up each one in a dish separately. In this connection I would remark that the same holds true of the colors produced by the Nessler reagent; for example, ten cc. of standard ammonium chloride is made up to 100 cc. and the reagent added. The colors produced by diluting one cc., five cc., or ten cc. of this (colored) solution to fifty each are not the same as those obtained by diluting 0.2

<sup>1</sup> *Lehrbuch d. Org. Chemie.*, 5th Ed'n., 572.

<sup>2</sup> Hazen, Report Mass. State Board of Health. "Purification of Sewage and Water," 1890, 712.

cc., one cc., or two cc. of the standard ammonium chloride solution each to fifty cc. and adding the Nessler reagent, but in every case darker.

The process is dismissed with the remark: "We have not been successful in so controlling the reaction as to get a constant product." The chief agents in the action of nitric acid upon any compound are heat and concentration. If, therefore, the dishes containing the residues are always at the same temperature,—which they must be, being at the temperature of the room—and the acid used of the same composition, it is difficult to see how the results could fail to agree in every case, and direct experiment proves this to be so, equal quantities of pure nitrate solutions agreeing exactly.

The investigation was conducted with reference to the following points:

#### I. ACIDS.

- a. Various acids.
- b. Method of treatment.
- c. Quantity of acid used.

#### II. EVAPORATION.

- d. Effect of sodium carbonate.
- e. Temperature at which it is carried on.
- f. Quantity evaporated.
- g. Effect of chlorine.

#### III. COMPARISON WITH STANDARDS.

The preparation of the phenolsulphonic acid is a matter of first importance, and for which, strange to say, no one has ever given definite directions. Kekulé<sup>1</sup> found when phenol and sulphuric acid were mixed, according to the temperature, varying amounts of ortho and para phenol monosulphonic acids were formed. As these could not fail to influence the action upon the dry-water residue, an acid of perfectly definite composition,—the pure disulphonic acid  $C_6H_4OH(SO_3H)_2$ , probably  $OH : SO_3H : SO_3H = 1 : 2 : 4$ , which with nitric acid gives *picric acid even in the cold*,<sup>2</sup>—has been mostly used in these experiments.

This is prepared as follows: three grams of phenol of good quality and thirty-seven grams of pure sulphuric acid sp. gr.

<sup>1</sup> *Ztschr. für Chemie*, 10, 199.

<sup>2</sup> Kekulé *Lehrbuch* III, 236.

1.84 (Kahlbaum's synthetic phenol and Baker and Adamson's "Strictly Pure" sulphuric acid were usually employed) are mixed in a flask and heated for six hours *in, not upon*, a water bath to 100°

To determine the number of sulphonic groups, a portion of this mixture was neutralized with barium carbonate, lixiviated with water, filtered, the filtrate evaporated and the barium salt recrystallized, giving handsome orthorhombic prisms. A determination of barium in this gave 35.16 per cent., the theory requiring 35.22 per cent. A determination of water of crystallization gave 15.66 per cent., theory, 15.62 per cent.  $H_2O$ . The acid as thus prepared may crystallize out upon standing, it being rather insoluble in the strong sulphuric acid, in which it forms supersaturated solutions. It may be brought into solution by reheating a short time, or by dilution with a small quantity of water, the undiluted acid has always been used.

The experiments were performed as follows: Two solutions were employed, one containing in one cc., 0.1000 part of nitrogen per 100,000 as potassium nitrate; the other in addition to this seven parts chlorine as sodium chloride per 100,000. Of these, portions of one cc. each were measured out and diluted to five and ten cc. with distilled water and evaporated in porcelain dishes.<sup>1</sup>

The  $2\frac{1}{2}$  inch evaporator containing the water residue was moistened with ten drops—0.7 cc.—of the phenolsulphonic acid, and by rubbing with a short glass rod every part of the residue covered with it; seven cc. of water are now added,—measured in later experiments by a Vanier<sup>2</sup> overflow pipette,—the solution stirred and three cc. ammonium hydrate, measured in like manner, added, the solution again stirred to insure uniformity, and the rods removed. In many cases the colors could be compared directly in the dishes, but in case of doubt the comparison took place in tubes about  $1\frac{1}{8}$  inches deep and  $\frac{5}{8}$  inch in diameter.

<sup>1</sup> A convenient way of marking these dishes is to remove a small patch of the glaze upon the outside of the dish by glass etching ink, leaving a rough surface for the lead pencil.

<sup>2</sup> *J. Anal. Appl. Chem.*, 2, 145.



Each determination is the average of at least two closely agreeing determinations.

All results are stated in parts per 100,000.

# I. ACIDS.

## (a) VARIOUS ACIDS.

Equal parts of phenol and } The colors obtained were brown and an accurate matching was impossible.  
sulphuric acids.

Unknown mixture of ortho and } The colors obtained were fairly good,  
para sulphonic acids from five } but in some cases were reddish  
per cent. solution of phenol. } tinted.

Pure ortho phenol mono- } This gave a precipitate with the ammonia and  
sulphonic acid.<sup>1</sup> } the colors were all bluish-green tinted.

Pure disulphonic acid, } The colors obtained were a pure yellow and  
7½ per cent. solution. } did not change upon standing. This, therefore, gives the best results.

## (b) METHOD OF TREATMENT.

*At 100°.*—Sprengel<sup>2</sup> states that the residue should be nearly at 100° when treated. Experiments performed by treating the residues upon the steam bath with the cold acid and also with the acid at 100° gave no better results than those obtained in the ordinary way.

*At 0°.*—Treatment of the chilled residues upon ice with ice-cold acid gave decidedly lower results than those obtained in the usual manner, the nitration probably not going as far.

*Addition of substances.*—The addition of phenol or phenolsulphonic acid to the water before evaporation is of no advantage whatever.

## (c) QUANTITY OF ACID USED.

If chlorine be absent or in small quantity, the amount of acid used makes very little difference. Enough should be used to cover the residue readily, usually ten drops=0.7 cc. is sufficient. For example, with equal quantities of the same nitrate solution which should have given a reading of 0.1000, the following results were obtained:

<sup>1</sup> Prepared by the cold evaporation in vacuo of the officinal solution of Merck's "Aseptol" and subsequent solution in sulphuric acid.

<sup>2</sup> *Pogg. Ann.*, 121, 188.

TABLE I.

Showing the effect of the quantity of acid used.

Without Chlorine.		With Chlorine, seven parts.	
10 drops acid.	6 drops.	10 drops acid.	6 drops.
0.0925	0.0900	0.0750	0.0700.

It is evident then that the use of too little acid causes the loss of nitric acid.

## II. EVAPORATION.

It is well known that certain salts in solution undergo decomposition when boiled. Fittig<sup>1</sup> found this to be true of ammonium chloride, Debbits<sup>2</sup> of several acetates with loss of acetic acid, and with the nitrate, sulphate, acetate and oxalate of ammonium with loss of the respective acids. Leeds<sup>3</sup> and Fox<sup>4</sup> have shown that nitrates are volatile at 100° and even lower temperatures.

In order to ascertain what the influence of the evaporation really was, the following experiment was tried:

An intimate mixture of dry finely powdered potassium sulphate and nitrate was made by grinding them together in an agate mortar for several hours. Sixteen portions of 100 milligrams each were accurately weighed out, each containing about 0.072 milligram of potassium nitrate. Twelve portions were dissolved each in ten cc. of water, four of these evaporated at 100°, four at 65°, and the remaining four at 20° over sulphuric acid.

TABLE II.

Showing loss of nitrate by evaporation at various temperatures.

	Dry.	20°.	65°.	100°.
I.....	0.1000	0.0890	0.0900	.....
II.....	0.1050	0.1000	0.1080	0.1160

The readings varied among themselves by 0.0200 and hence were averaged.

To obviate this variation, sixteen portions of one cc. each of a nitrate solution were measured out, nine cc. of water added and all allowed to evaporate over sulphuric acid at a temperature of 20°. Ten cc. of water were added to each one of twelve of

<sup>1</sup> *Ann. Chem. Pharm.*, 128, 189.

<sup>2</sup> *Ber. d. chem. Ges.*, 5, 820.

<sup>3</sup> *Am. J. Sci.*, (3) 7, 197.

<sup>4</sup> *Tech. Quarterly*, 1, 1.

these, and four evaporated at 20°, four at 65°, and four at 100°; this gave a series in which exactly the same amount of nitrate in every case was spread uniformly over the dishes and had been subjected to these various temperatures.

TABLE III.

Showing loss of nitrate by evaporation at various temperatures.

Dry.	20°.	65°.	100°.
0.1000	0.0990	0.0965	0.0990

These results indicate that there is a loss of about one per cent. when the water is allowed to evaporate at ordinary temperatures over sulphuric acid, or in a steam bath where it evaporates rapidly and is *immediately* removed; at 65° where the evaporation is slower, and the time of exposure to heat consequently lengthened, the loss is greater, in this case about three and a half per cent.

(d) EFFECT OF SODIUM CARBONATE.

With a view of fixing the nitric acid and thus diminishing the loss by evaporation, it has been suggested that carbonate of sodium be added to the water before evaporation; as carbon dioxide is given off upon treatment with acid, it is possible that this carries off with it a slight quantity of nitric acid. Ten portions each of nitrate solution, the reading of which should have been 0.1000, were evaporated, the average reading was 0.0970, with the addition of soda 0.0973. Ten portions each of the same solution, containing in addition seven parts chlorine per 100,000, when similarly treated gave 0.0821, with the addition of soda 0.0812.

The avidity of acetic acid being much less than that of nitric acid, added to the fact that it was non-volatile at the temperatures employed, led to the suggestion that some of its salts be employed as a substitute for the sodium carbonate. Sodium acetate when added to the water, gave rather lower results than those obtained when it was not used.

(e) TEMPERATURE AT WHICH EVAPORATION IS CARRIED ON.

The accompanying table shows clearly the effect of temperature upon the determination.

The solutions should have all read 0.1000 part nitrogen as

potassium nitrate per 100,000, they were all treated with carbonate of sodium and each figure represents the mean of two closely agreeing determinations.

TABLE IV.

Effect of temperature.

Pure niter solution.

Temp.	Quantity evaporated.		
	1 cc.	5 cc.	10 cc.
100°.	0.0925	0.0920	0.0920
65°.	0.0890	0.0890	0.0880
20°.	0.1050	0.0980	0.1000

Niter solution with 7.0 parts chlorine.

Temp.	Quantity evaporated.		
	1 cc.	5 cc.	10 cc.
100°.	0.0680	0.0700	0.0600
65°.	0.0650	0.0650	0.0680
20°.	0.0935	0.0920	0.0700

It is evident that there is a decided loss of nitrate when evaporation takes place at 65° (the temperature which water assumes in a porcelain dish when upon the top of a water bath) over that lost at 100° and here even over that lost at 20°. With chlorine this is even more perceptible; the reason for the increased loss at 65° is probably, as already stated, that the time of exposure at this temperature is longer.

It is important, however, that the dishes be removed as soon as dry, as the subsequent exposure causes loss of nitrate.

TABLE V.

Effect of heat upon the dry residue.

Water contained 0.1000 part N as  $N_2O_5$ , 7.0 part Cl.

	Quantity evaporated.		
	1 cc.	5 cc.	10 cc.
Removed at once.....	0.0750	0.0710	0.0740
Exposed half an hour at 65°..	0.0700	0.0625	0.0690

(f) QUANTITY OF SOLUTION EVAPORATED.

The quantity of solution evaporated seems to exercise but slight influence upon the results, although the smaller it is, the less the loss; this is evident from all three of the preceding tables.

(g) EFFECT OF CHLORINE.

The presence of large quantities of chlorides in the water does

unquestionably lower the results. If the process be conducted in the usual way, by the evaporation of ten cc. at  $100^{\circ}$  it shows in Table IV, a loss of from thirty to forty per cent. of nitrogen as nitrate. If a smaller quantity, five cc. or even one cc., be used, and the evaporation be carried on at  $20^{\circ}$  over sulphuric acid, this loss is reduced to six or seven per cent., and of this probably one half is due to unavoidable errors in matching the colors.

If the chlorine amounts to but 2.0 parts per 100,000, which is perhaps high in waters of doubtful character, it exercises practically no influence.

TABLE VI.

Effect of 2.0 parts of chlorine (as NaCl) per 100,000. Readings should be 0.1000.

	1 cc.	10 cc.
$100^{\circ}$ .	0.0900	0.0900 (average of five determinations.)
$65^{\circ}$ .	0.0900	0.1000
$20^{\circ}$ .	0.0975	0.1050

### III. COMPARISON WITH STANDARDS.

The yellow color of the picrate solution when as high as 0.1000 is extremely hard to match accurately; the tints must be read off at once without any delay as the difficulty increases with the time spent in comparison. It is well after reading perhaps a dozen, to rest the eyes by looking intently at a piece of blue paper.

As a result of a long series of experiments upon three different people,—all experts in the comparison,—it was found that the error of reading colors up to 0.0500 part N as  $N_2O_5$  was 0.0020 or 0.0030; up to 0.1000 part N as  $N_2O_5$  was 0.0050.

No advantage was gained by the use of colored glasses or, when the colorimeters were used, of colored papers underneath them.

The process does not, as stated by Grandval and Lajoux,<sup>1</sup> and also in Graham-Otto,<sup>2</sup> estimate the nitrogen present as nitrites; this is clearly impossible, as the action of nitrous acid upon phenolsulphonic acid results in the formation of nitrosophenol

<sup>1</sup> *Compt. rend.*, 101, 6a.

<sup>2</sup> *Lehrbuch d. anorgan. Chem.*, 2, Part 1, 200.

$C_6H_5NO_2$  which is colorless in dilute solutions. This view was supported by an experiment with pure sodium nitrite prepared from pure silver nitrite, in which no color whatever was obtained upon treatment with the phenolsulphonic acid.

The results of this paper may be summarized as follows:

The most satisfactory manner of execution is,—in the case of a water high in nitrates,—to use that quantity which will give a reading of about 0.0700 when one or two cc. are employed; in the case of ground water ten cc. of a portion which has been decolorized by the use of alumina in the cold, is evaporated upon the water bath, the dish being placed in the steam and removed *as soon as dry*, or better, when a drop is still remaining. In case the chlorine be high, which often accompanies high nitrates, this evaporation had best take place in vacuo over sulphuric acid, and the chlorine, if it exceeds 7.0 parts per 100,000, removed by silver sulphate which has been proved to be free from nitrate.<sup>1</sup>

In case one or two cc. of the water is used the 0.7 cc. of acid used is sufficient to cover the residue completely.

The error of reading up to 0.0500 is 0.0020 or 0.0030, four to six per cent. Up to 0.1000 is 0.0040 or 0.0050, four to five per cent., but the process as here described is more trustworthy, delicate and accurate than any process yet published.

For easy comparison 0.720 gram  $KNO_3$  can be dissolved in one liter of water, ten cc. of this allowed to evaporate in vacuo, treated with acid, made up to a liter and portions as wanted made alkaline with ammonia, of this ten cc. = 0.1000 part nitrogen as potassium nitrate per 100,000.

*Acknowledgment.*—The writer would hereby acknowledge his indebtedness to Prof. Drown and Mrs. E. H. Richards, chemists to the Massachusetts State Board of Health, for hints and suggestions, and to Miss Isabel F. Hyams and Mr. H. C. Tuttle, also of the Board of Health staff, for valuable assistance in making many of the readings involved in the preceding work.

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<sup>1</sup> Samples from E. Merck, marked "C. P.," contained enough nitrate to vitiate all results.

## EXPERIMENTS ON THE ANALYSIS OF PIG COPPER, BRASSES, AND BRONZES.

BY JAMES S. DEBENNEVILLE.

Received January 27, 1894.

**I**N a recent number of this JOURNAL (January, 1894) a preliminary note was given on a method for systematic examination of pig copper and high copper percentage alloys. It is proposed in this paper to present some of the experiments involved in the work of which the note was a résumé. The results are familiar to those working in copper analysis, but on taking up the subject I was not able to find in the literature accessible to me quantitative data of many current statements. It is known, for instance, that in determining tin in copper alloys by solution in nitric acid that phosphorus and arsenic remain in their oxidized forms with the metastannic acid but it was sought to ascertain whether the reaction was quantitatively exact or whether phosphorus and arsenic were still to be looked for in the filtrate from the residue.

Taking up tin the question was as to how that metal alloyed with copper reacted during analysis. The usual method of determining tin in such alloys is by solution in nitric acid, evaporating off excess of acid, diluting and when the precipitate has settled, filtering. The points to be taken into consideration are:

1. Whether or not the metastannic acid formed is soluble in nitric acid. Experiment answers this negatively.
2. Whether or not the metastannic acid is soluble in ammonium hydroxide, ammonium nitrate, or both. Experiment answers this also negatively.
3. The state of purity in which the residue is obtained. It is a matter of experience that in nitric acid solution, especially when evaporated to a point where basic salts are liable to form, the stannic oxide is found to be more or less contaminated with such salts of copper, manganese, and iron. These impurities adhere most tenaciously and washing with dilute nitric acid will not remove them completely. The reaction of tin phosphate and arseniate holds quite rigidly. The attack on tin by nitric acid is a solution and conversion into

an oxidized form and in this reaction if phosphoric or arsenic acids be present the stannic phosphate or arseniate is formed which, like the bismuth salts, is insoluble in nitric acid of five per cent. or less strength. The importance of this reaction in copper analysis is very great. With the exception of certain special alloys the tin present will generally exceed the quantity necessary to hold the arsenic and phosphorus in an insoluble form and the phosphate and arseniate of tin are not readily decomposed by simple digestion with alkali sulphide ( $S_n$ ) but require fusion.

The following experimental results were obtained. Expressed in grams or fractions thereof. The term "metastannic acid" is used to indicate the residue obtained on dissolving tin in nitric acid, but such residue also contains stannic acid.

I. Solubility of the metastannic acid or residue obtained on dissolving pure tin in nitric acid. Excess of acid removed by evaporation to pasty condition. Dilution forty cc. Filtered after twelve hours.

Tin taken.....	1368	1544	1610	1744	1623	1674
Tin found.....	1365	1557	1620	1745	1630	1683

II. Solubility of the metastannic acid or residue obtained. Dissolving the tin in excess of nitric acid. Present 6.92 free nitric acid. Dilution 150 cc. Filtered after twelve hours.

Tin taken.....	1812	1734	1795	1808	1746
Tin found.....	1812	1738	1792	1800	1732

III. Solubility of the metastannic acid or residue obtained. Dissolving in nitric acid. Evaporating to paste. Diluting to forty cc. and digesting twelve hours with five grams ammonium nitrate.

Tin taken.....	1963	1822	1763	0600	1814	1280
Tin found.....	1965	1842	1784	0602	1839	1301

IV. Solubility of the metastannic acid or residue obtained. Conditions as in III. Digesting twelve hours with 6.52  $NH_3$ .

Tin taken.....	1653	1472	1785	1530	1671	1242
Tin found.....	1679	1498	1808	1563	1690	1260

V. Solubility of metastannic acid or residue obtained. Conditions as in III and IV. Digesting twelve hours with five grams  $NH_4NO_3 + 6.52 NH_3$ .



Tin taken.....	1495	1527	1357	1731	1567	1511
Tin found.....	1534	1567	1408	1784	1606	1546

VI. Precipitation of tin by  $\text{NH}_4\text{HO}$ . Five grams of copper present 6.92 free  $\text{HNO}_3$ . Ammonia added at once to re-solution of the copper salt. Filtered after twelve hours. All contaminated with copper oxide. Washed with dilute nitric acid.

Tin taken.....	1986	1770	1779	1928	1977
Tin found.....	2095	1907	1866	1998	1958

VII.  $\text{P}_2\text{O}_5$  remaining with metastannic acid. Excess of tin present. Phosphor-tin treated with nitric acid. Evaporated to paste. Dilution forty cc. Present 0.0631 phosphorus in one gram.

Phosphor-tin taken.....	3150	2580	2763	2400	0990
P in filtrate .....	0003	trace	trace	0004	trace
Per cent. P in residue ...	99.905	....	....	99.983	....

VIII.  $\text{P}_2\text{O}_5$  remaining with metastannic acid. Excess of phosphorus present. Conditions as in VII. Present 0.0250 phosphorus.

Tin present.....	0078	0076	0067	0077	0075
P combined .....	0190	0146	0131	0151	0154

The ratio of  $\text{SnO}_2$ :  $\text{P}_2\text{O}_5$  is 1: 4 (on averaging).

IX.  $\text{As}_2\text{O}_3$  remaining with metastannic acid. Excess of tin present. The arsenic and tin treated with nitric acid. Conditions as in VII. Present 0.0067 arsenic.

Arsenic in filtrate .....	0012	0009	0011	0012	0011
Per cent. As in residue ....	83.5	86.6	83.6	83.6	83.6

X.  $\text{As}_2\text{O}_3$  remaining with metastannic acid. Excess of arsenic present. Conditions as in IX. Present 0.0134 arsenic. In filtrate.

Arsenic .....	0129	0121	0129	0107	0113
Per cent. loss .....	3.73	11.19	3.73	20.15	15.67

In both IX and X tin and arsenic were attacked by nitric acid in presence of each other. In IX there was a large excess of tin (0.1000 gram). In X there was 0.0095-0.0110 tin present. The operations were conducted in the same manner and repeated.

XI. Phosphate of tin with metastannic acid. Digested at  $70^\circ$  for five hours with excess  $\text{Na}_2\text{S}$ .

Phosphorus present.....	0071	0046	0069	0061	0136
P as unconv'd phosphate ..	0024	0018	0041	0037	0114
Per cent. unconverted.....	33.8	37.1	59.4	60.3	83.8

No 5. (83.8) in solution in nitric acid was inadvertently carried to complete dryness.

XII. Arseniate of tin with metastannic acid. Digested at  $70^{\circ}$  for five hours with ammonium sulphide. Filtered from residue after twelve hours. Present 0.0067 arsenic.

As as unconv'd arseniate ..	0051	0057	0055	0058	0057
Per cent. unconverted.....	76.12	85.07	82.09	86.56	85.07

The residue, acids of tin, were converted by ignition in a porcelain crucible, to stannic oxide. The full heat of a Fletcher lamp was used. Phosphorus was precipitated by molybdic solution and weighed as  $Mg_3P_2O_8$ . Arsenic was weighed as  $Mg_3As_2O_8$ .

With antimony a number of similar experiments were carried out. The antimony was weighed as  $Sb_2O_3$  and  $Sb_2S_3$ .

XIII. Solubility of the residue obtained by dissolving pure antimony in dilute nitric acid (1-3) evaporated to pastiness. Dilution forty cc. Filtered after twelve hours.

Antimony taken .....	1004	1186	1198	1243	1120
Antimony found .....	0947	1151	1170	1232	1017

XIV. Residue as in XIII. Nitric acid solution containing 6.92 free nitric acid. Dilution 150 cc. Filtered after twelve hours.

Antimony taken .....	2214	2166	2244	2600	2277
Antimony found .....	2046	1829	2079	2537	2160

XV. Residue as in XIII. Digested twelve hours with 6.52  $NH_3$ . Dilution forty cc.

Antimony taken .....	1012	1000	1584	1278	1100
Antimony found .....	0982	0965	1551	1272	1038

XVI.  $P_2O_5$  remaining with the oxides of antimony on solution of metallic antimony in nitric acid. Excess of antimony present. Evaporated to pastiness. Dilution forty cc. Present 0.0051 phosphorus.

Phosphorus in filtrate....	0020	0033	0018	0018	0015
Per cent. P in residue ...	60.78	35.29	64.70	64.70	70.59

Antimony is a most troublesome determination to make in copper analysis. If it can be separated and obtained in a precipitate of small bulk the solubility of the sulphide in alkali sulphide can be taken advantage of, but to apply this reaction in

the presence of ten to twenty grams of copper in the form of an easily oxidized sulphide is a difficult and tedious operation.

The object of the use of ammonia and barium hydrate is to effect for copper what is done in iron analysis for single determinations. In separating manganese or phosphorus in a steel one of the objects is to retain the iron in solution, precipitating out the element which is present only in small quantity. The bulk of the copper being held in solution by the ammonia and precipitation being completed by barium hydrate the analysis of a pig copper is simplified by having a small precipitate to work upon. An excess of barium hydrate being used the separation of the crystalline barium carbonate probably has its effect in the filtration. If we have to make a systematic examination of a copper alloy, as in any case the residual tin oxide obtained by the nitric acid method would have to be purified, it is easier to do this work of purification and separation in such a way as to obtain quantitative results of the different minor constituents sought. If there is enough iron, tin, etc., to fix all the phosphorus and arsenic in an insoluble form the results are quantitative for these elements. To add ferric chloride to obtain such results may be of advantage, but iron is an important object of search in such examination and these two elements are not difficult to separate from the main bulk of copper by other methods. Only special alloys, such as phosphor-bronze or a manganese-copper alloy made with ferro-manganese contain notable quantities of phosphorus. Phosphorus is also sometimes present in aluminum brass, and a sample was found to contain 0.056 per cent. P to 0.22 Fe. Where phosphorus and arsenic are used as deoxidizers, only a very small quantity is to be found on analysis.

To properly precipitate iron, aluminum, or bismuth by ammonia it is necessary to avoid a large excess of the reagent, but in adding ammonia to re-solution of the copper salt an excess must be added and retained. Using test solutions for examination of the use of ammonia and barium hydrate the following results from sixty odd experiments were obtained:

Element.	NH <sub>4</sub> HO.	NH <sub>4</sub> HO+Ba(HO) <sub>2</sub> .	Dilution.
Phosphorus.....	not precipitated.	{ not precipitated completely.	100 cc.
Arsenic .....	"	precipitated.	50 cc.
Nickel .....	"	not precipitated	"
Cobalt. ....	"	"	"
Zinc .....	"	"	"
Cadmium .....	"	"	"
Silver .....	"	"	"
Bismuth.....	ppt. incomplete.	ppt. complete.	150 cc.
Manganese .....	"	"	"
Antimony .....	"	{ coloration by H <sub>2</sub> S, trace in solution.	"
Tin.....	ppt. complete.	ppt. complete.	"
Lead .....	"	"	"
Iron.....	" (?)	"	"

With arsenic in the ammoniacal solution of fifty cc. dilution the precipitation by Ba(HO)<sub>2</sub> is complete, as barium ammonium arseniate (Douglass and Prescott, Qual. Anal.). In dilute solutions or on heating the precipitation becomes incomplete. Digestion with alkali sulphide (S<sub>n</sub>) does not transpose this precipitate. Phosphorus is precipitated as barium phosphate. With a copper containing known quantities of the minor constituents the following results by the use of ammonia and barium hydrate were obtained: The original copper taken contained 0.03 per cent. Fe and 0.025 per cent. Pb as impurities. Allowance was made in calculating.

Element.	Present.	Taken 10 grams	Taken 20 grams	Taken 30 grams	Taken 40 grams	Taken 50 grams
		Cu	Cu	Cu	Cu	Cu
Arsenic .....	0079	0053	0051	0081	0079	0073
Tin .....	0041	0048	0043	0043	0030	0040
Antimony ....	0048	0051	0050	0042	....	0045
Lead .....	0053	0052	0056	0056	0060	0057
Bismuth .....	0028	0030	0030	0026	0029	0034
Cadmium .....	0295	0309	0307	0291	....	0221
Phosphorus...	0032	0024	0037	0029	0021	....
Dilution in cc. ....		300	400	(800)	800	800

The difficulty arising in the use of thirty, forty, or fifty grams of the pig copper came from the separation of the copper-ammonium salts. The dilution was 800 cc. It also takes the equivalent quantity of potassium cyanide to decolorize the filtrate. If

the solution is allowed to stand but thirty to sixty minutes the copper salt is much diminished in quantity and the precipitate appears to be all down. Ten grams and a dilution of 150 cc. works well. The copper-ammonium salts are readily soluble in water on warming, and if arsenic and phosphorus are in the form of iron or other insoluble salt they are not affected by such treatment. The above results were obtained: By dissolving in nitric acid, adding ammonium hydroxide to re-solution of the copper salt followed by addition of excess of barium hydroxide, such excess being quickly indicated by the formation of the crystalline barium carbonate. Allowed to stand 30 to 120 minutes and filtered. Filtrate decolorized by potassium cyanide and precipitated by hydrogen sulphide.

In the July (1893) number of this JOURNAL Mr. Jesse Jones applies a method for the determination of manganese in bronzes based on Ford's method in steel analysis. In the course of the method as described he removes copper by hydrogen sulphide, filters and obtains the manganese from the filtrate. His paper simply describes the course of analysis without entering into any details as to why it was found necessary to remove the copper. In making some analyses for Mr. F. Lynwood Garrison (*Jour. Frank. Inst.*, June to September, 1891), Hannay's reaction, the oxidation and precipitation of manganese as manganese dioxide in the nitric acid solution by potassium chlorate, was applied at once and without removing copper. It was the suggestion of the late Dr. F. A. Genth to try this method as conducted in the analysis of steel and subsequent examination of the filtrate gave negative results for manganese. I have repeated the experiments to find out whether or not removing copper is a source of error and the results given below were obtained on a manganese brass, dissolved in nitric acid and made up to 100 cc. Aliquot portions were then taken, the manganese precipitated by potassium chlorate and titrated in neutral solution by permanganate. The variation is within reasonable limit and shows, I think, that there is no objection to proceeding with a copper alloy in the manner as with steel and that the removal of copper is not essential to accuracy.

00659

00659

00655

00647

00655

00640

I wish to acknowledge the kindness of Prof. F. A. Genth to whose encouragement was largely due the idea of putting these data into form, and of Mr. F. Lynwood Garrison to whom I am indebted for a number of alloys from his collection.

CHEMICAL LABORATORY,  
123 S. SEVENTH ST., PHILADELPHIA, PA.

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## INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

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### SUB-COMMITTEE ON METHODS.

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#### BULLETIN No. 1.

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#### ORGANIZATION AND WORK OF THE COMMITTEE.

AT the World's Congress of Chemists, in Chicago, last August, following the papers of Professor J. W. Langley, "On the Work of the Committee on International Standards for the Analysis of Iron and Steel," and of Dr. C. B. Dudley, "On the Need of Standard Methods for the Analysis of Iron and Steel, with Some Proposed Standard Methods," was a brief discussion, which resulted in the reference by that body of the whole subject of standard methods for the analysis of iron and steel, to the Committee on International Standards for the Analysis of Iron and Steel. That committee, it will be remembered, consists of seven chemists, in each of five different countries, namely, England, France, Germany, Sweden, and the United States. The American Committee was appointed jointly by the American Society of Civil Engineers, and the University of Michigan, with Professor J. W. Langley, Case School of Science, Cleveland, Ohio as Chairman. The other members of that Committee were W. P. Barba, Midvale Steel Works, Nicetown, Philadelphia, Pa., A. A. Blair, 406 Locust street, Philadelphia, Pa., Professor Regis Chauvenet, President State School of Mines, Golden, Colorado, Professor T. M. Drown, Mass. Inst. Technology, Boston, Mass., Dr. C. B. Dudley, Chemist Penn'a. R. R. Co., Altoona, Pa., and Porter W. Shimer, Easton, Pa.

Following the reference of the subject to this committee, it

was decided after consultation to appoint a sub-committee, to take up the question of standard methods. The sub-committee is constituted as follows: W. P. Barba, A. A. Blair, T. M. Drown, Porter W. Shimer and C. B. Dudley, Chairman.

The sub-committee held an organizing meeting at the office of A. A. Blair, 406 Locust street, Philadelphia, on December 13, all the members being present. The object of the meeting was to map out the work. It was agreed as follows:

First. That Mr. Blair should submit a form of circular to go to the iron and steel chemists of the country, asking for a brief outline of the methods which they prefer, and the reasons for all the important points of their methods.

Second. That the work of the committee should comprehend the recommendation of standard methods to be used as the basis of commercial transactions, and when any of these methods could not be used in steel works in daily practice, on account of time required, an alternative rapid method should be recommended, and its limitations defined.

Third. That the members of the committee should draw up each proposed standard method in writing, with some minuteness, and give the reasons for each important point, these written drafts to be sent to the chairman, to be duplicated, and sent to every member of the committee. Later, the points agreed upon are to be edited by some one member of the committee.

Fourth. That only one element should be embraced in a method.

Fifth. That the first method to be taken up, should be phosphorus in steel.

Sixth. Mr. Barba offered to furnish to each member of the committee, a suitable quantity, not less than a pound or so, of borings of three (3) different kinds of steel, namely, one of from 0.01 to 0.02 phosphorus, carbon about 0.90, and silicon about 0.40; another with phosphorus not far from 0.06, carbon 0.50 to 0.60, silicon 0.25 to 0.30, and arsenic 0.15 per cent. The above two, to be crucible steel. Another sample of open hearth steel of carbon 0.90 to 1.05, phosphorus 0.02 to 0.04, manganese 0.30 to 0.40, silicon 0.20 to 0.25, sulphur 0.02 to 0.04 and copper anywhere below 0.10.

Seventh. Dr. Dudley offered to furnish to each member of the committee, a like amount of borings from a sample of Bessemer steel of from, 0.10 to 0.12 phosphorus, carbon about 0.50, manganese 0.80 to 1.00, silicon 0.02 to 0.05, sulphur 0.07 to 0.10 and copper from 0.07 to 0.10. These samples of steel to be used in deciding various questions that may come up in regard to proposed methods.

A very earnest feeling was manifested at the meeting of the sub-committee, and the outlook for some good work, is apparently very favorable.

APPROVED:

J. W. LANGLEY,

CHAS. B. DUDLEY,

*Chairman Sub-Committee.*

*Chairman Com. on Int. Standard.*

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### NEW BOOKS.

A MANUAL OF PRACTICAL ASSAYING. BY H. van F. FURMAN.

The constantly increasing demands made on metallurgical chemists for rapid work makes the appearance of Mr. Furman's book very timely; for while there are numerous text-books on assaying, and complete treatises for the iron-works chemist, no work until this has so completely embodied the methods now in use by the chemists of the silver, lead, and copper smelters of the west, and it is for these especially that the book is written.

On this account it would seem more appropriate to have included technical analysis in the title, for while the term assaying may doubtless be properly used as meaning more than fire assaying, it can hardly be construed into covering the contents of this book, which contains methods not in common use, by the technical chemist at least, and which in actual practice would probably be looked up in more detailed and specialized works. It would, however, hardly be just to criticise the author for making his manual as complete as possible, providing good judgment is used in selecting the methods, which is the case in all but a very few instances.

Part I, which is introductory, and includes chapters giving useful details as to reagents, apparatus, blowpipe reactions, etc.,



contains a chapter on sampling worthy of special mention. This chapter gives a thorough description of both hand and mechanical sampling as applied to the crude material, and to the finished products of the smelter. When it is remembered that the value of all the subsequent work depends upon having a good sample to start with, it can easily be seen that a knowledge of this subject is of great importance. As those accustomed to smelter work know, inaccurate sampling, either real or supposed, is the source of constant disputes; and anyone not already familiar with the various methods can read this chapter with profit.

Part II describes the methods for the separate determination of all the elements which need be considered in a technical manual; including a very full description of the fire assay for gold, silver, and lead.

Of course in a limited space no review can be attempted of all the methods given in this part of the book; but in general it can be said, that while there are perhaps occasional details which could be advantageously modified, they are methods which have stood the test of actual use under the trying conditions of smelter laboratories, where rapidity is the first and accuracy the second essential.

Some of the methods given here, while in constant use in the west, have not received the attention they deserve at the hands of analytical chemists in general; most conspicuous of these are the methods of A. H. Low for zinc, of H. H. Alexander for lead, and of F. C. Knight for lead, when used with the skill coming from practice, and with a proper understanding of the conditions involved, these methods, while essentially rapid, give results of a high degree of accuracy; they have a place indeed in the first rank of volumetric determinations.

The student of technical analysis can safely accept the methods given in Part II as carefully selected and reliable, and rendered additionally valuable by the liberal use of foot notes in referring to the original sources of information.

Part III is devoted to the description of special assays and analyses. The most important chapters here of course are those dealing with subjects which come up with more or less con-

stancy in smelter laboratories and assay offices; such as the assaying of the different kinds of bullion and mattes, and the analysis of slags, and these the author has treated very satisfactorily. In addition, among somewhat miscellaneous matter, are chapters on the analysis of gases, water, phosphates, etc., which in the absence of the standard text-books on these subjects will furnish a guide for doing such work, although the practice of trying to do chemical work without the proper fundamental knowledge cannot be too strongly deprecated.

Part IV, the last, includes chapters on the writing of chemical equations and stoichiometry, which are good in themselves, but of doubtful usefulness in a book of this kind, unless, perhaps, they are considered chiefly as preparing the way for the final chapter on the calculation of lead blast-furnace charges; a subject of much importance, and one which the author, from his own experience, is well fitted to treat.

A copious and well selected set of tables concludes the volume.

In his expressed object to "fill \* \* the wants of technical chemists" the author has certainly succeeded quite well, perhaps even too well; for with a volume of condensed information at hand the race of "machine" chemists, with which the west is already overstocked, will probably be increased. For this evil some of the western technical schools are primarily to blame. So long as they see fit to give a student a certificate of competency as a chemist or assayer when his stock of knowledge consists of an assortment—well selected it is true—of rule-of-thumb methods, just so long will the demand for this kind of education exist; and Mr. Furman, I fear, has unintentionally made it easier to get. While his book will be most useful to the well-trained analyst who can use the methods with discrimination, it can also be made to answer the purpose of the mechanical chemist as well.

L. G. EAKINS.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### NEW YORK SECTION.

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### PAPERS READ.

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#### AUTOMATIC ZERO BURETTE.<sup>1</sup>

BY EDWARD R. SQUIBB, M. D.

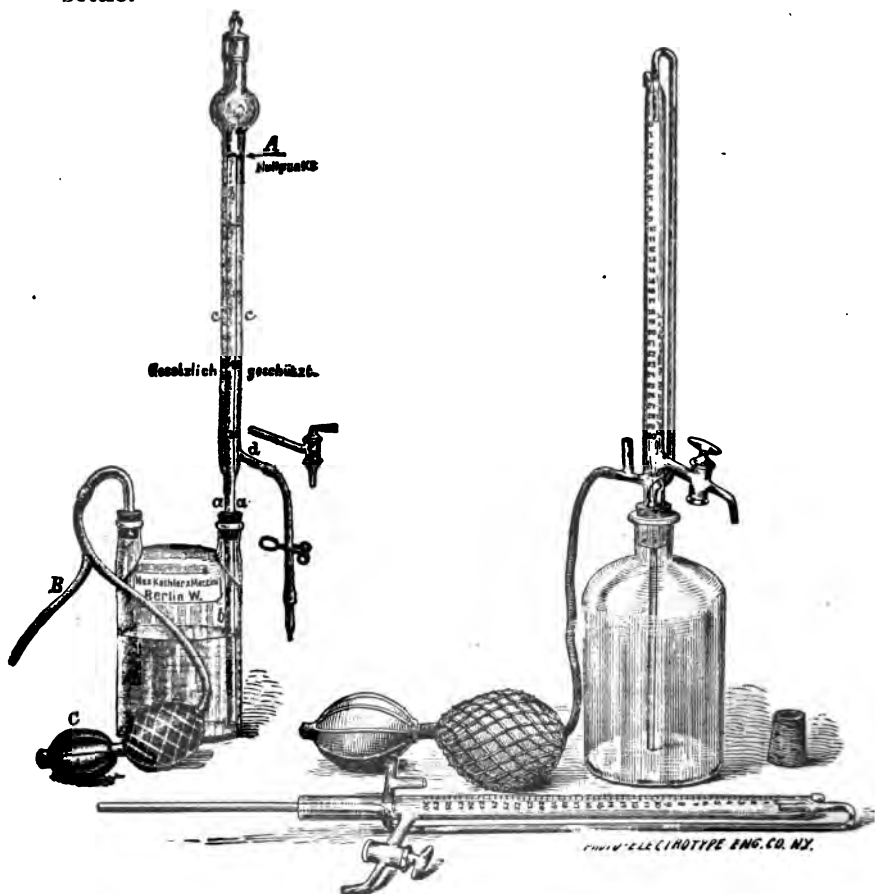
IN many manufactories and laboratories two or more volumetric solutions are in frequent use, and for such it is convenient to have a burette that can be rapidly used, and be carried about from place to place. This is practicable with the ordinary burette and stand. But then the bottle of volumetric solution has also to be carried about and much time is required in filling and adjusting to the Zero mark.

In the *Berichte der deutschen chemischen Gesellschaft* for October 24, 1892, No. 15, page 3010, Stanislaus Krawczynski has a description and cut of a new form of burette with an arrangement for automatic or mechanical filling to the zero point. The cut of this apparatus is reproduced here in the left-hand group of the first illustration plate in order that the inventor may have due credit for the physical principles of which he has availed himself.

On having a couple of these made for trial the writer observed that solutions of different physical properties gave different levels in overflowing through the central tube and were not fairly constant to the zero mark. Messrs. Eimer and Amend, of New York, had one made in which the internal tube was turned over upon itself for about one cm. at the upper end and this gave a

<sup>1</sup> Read December 8, 1893.

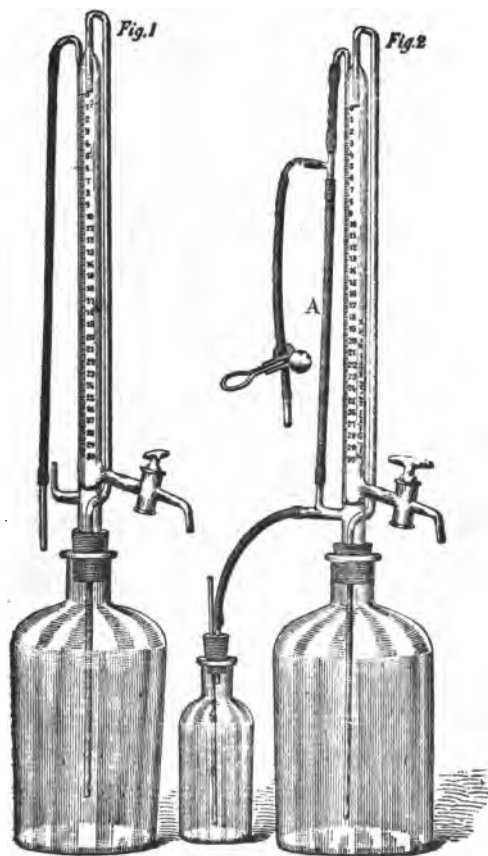
more uniform level with different solutions; and they substituted an ordinary Erlenmeyer flask of liter size for the two necked bottle.



But it was found impracticable to get the internal tube quite straight, and to have it exactly in the center of the outer graduated tube throughout its length, and the least variation in this condition gave a distorted meniscus. Then again the distortions were not uniform nor constant, but varied with the relations between the inner and outer tubes so as to disturb the values of the readings in different parts of the burette.

To overcome these disadvantages this writer simply put the filling tube from the bottle on the outside of the burette in the way shown in the right-hand group of the illustration. By this arrangement the excess of liquid blown over by the rubber pressure bulbs is siphoned off to the zero point with a fair degree of accuracy and uniformity after the finger is removed from the open end of the **L** tube on the left.

After a little experience with this modification it was easy to reach another that had still greater advantages over the last. In this the expensive and cumbersome rubber pressure bulbs are



dispensed with, and the burette is filled by mouth-suction, just as an ordinary pipette is filled. The apparatus shown by Fig. 1, of the second cut shows this design in its simplest form. Here the suction is applied at the top of the burette, the filling liquid rising from the bottle through the outside tube until the zero mark is passed. Then on stopping the suction the excess of solution is siphoned off to the zero mark and flows back into the bottle. If the apparatus is to be set aside for any considerable length of time it may be closed against the external

air by removing the glass mouth-piece from the suction tube,

and slipping the end of the rubber tubing over the turned up end of the glass tube by which air is admitted to the bottle to replace the solution drawn up the filling tube. But this is hardly necessary in any ordinary usage.

In many cases, however, it is necessary to exclude the carbon dioxide and other impurities of the laboratory air from volumetric solutions, and to prevent concentration of the solutions by evaporation of their water. These conditions are met in the modification shown in Fig. 2, of the second cut. Here a small wash-bottle is added, through which all the air admitted to the apparatus, either above or below, must pass, and be washed in passing. This bottle may be supplied with baryta water or lime water when it will serve to saturate the air through it with moisture, and free it from ordinary gases and vapors. In using this apparatus a pinch-cock is necessary on the rubber suction tube near the mouth-piece, by which the mouth-piece is conveniently handled, and during the suction this pinch-cock is opened and the rubber tube below is pinched at A by the thumb and finger of the left hand. This apparatus is constantly sealed from the external air, and is safe and accurate for any length of time, and is always in readiness for use, care being taken to well wash the end of the stop-cock, and to waste the solution that is outside of the cock whenever the apparatus has stood unused for even a few hours.

These burettes are very well made by Mr. Emil Greiner, of 146 William Street, near Fulton, New York City, who supplies them with or without the bottles as ordered. The only advantage in ordering the burette and bottle together is to have the internal tube of the right length to reach the bottom of the bottle.

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### A COMPRESSED AIR WASH-BOTTLE.<sup>1</sup>

By W. C. FERGUSON.

THIS idea, not yet put in practical operation, was suggested by the difficulty attending the washing of such precipitates as hydrate of alumina, the complete removal of very small amounts of finely divided material from the sides of the contain-

<sup>1</sup> Read December 8, 1893.

ing vessels, such as gold in commercial copper, or of such precipitates as adhere with persistency, when the ordinary wash-bottle, with comparatively little pressure available, is used. It would also seem that such a device would facilitate the general washing of precipitates in a laboratory where sometimes a hundred or more filtrations are made in a single day.

The features of the idea are about as follows:

Compressed air would be the source of pressure, and in the laboratory of which the writer has charge it could be introduced very conveniently from the factory where it is used on a large scale. Mr. J. B. F. Herreshoff, the distinguished chemical engineer, suggested using a gasometer where no source outside of the laboratory was available.

The air pipe would be arranged with branches to the filter pumps, and also to any other part of the laboratory where filtrations would be carried on.

The wash-bottles would be large and stout, and the apparatus arranged so that they could be removed readily and refilled or replaced as required. The air pipes would be provided with stop-cocks, just above the bottle, for regulating the supply of air. Glass nozzles of about the same form and length as in the ordinary wash-bottle, but with orifices of different sizes would be used, so that a very fine jet or a large stream of water could be employed as desired.

Rubber tubing of suitable length and strength would connect the water-bottle and nozzle.

The jet would be further regulated by a pinch-cock just above the nozzle so as to be conveniently manipulated while washing.

The advantages of this device would seem to be a minimum amount of work in manipulation, and a more thorough washing due to increased pressure. Where a large amount of work is done each day and accurate, prompt reports are absolutely necessary, it is self-evident that all devices that reduce labor and in other ways increase efficiency, tend to raise the standard of results.

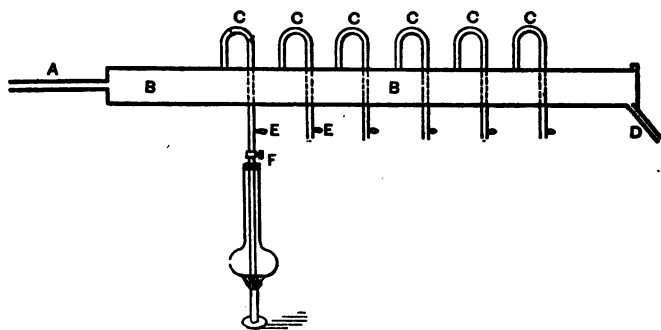
## AN ARRANGEMENT FOR CONDUCTING A NUMBER OF LABORATORY DISTILLATIONS WITH STEAM, SIMULTANEOUSLY.<sup>1</sup>

By W. C. FERGUSON.

A is an ordinary  $\frac{3}{8}$  inch iron steam pipe connected with the steam system in the factory and provided with a valve where it enters the laboratory. B is a brass pipe  $1\frac{1}{2}$  inches in diameter, connected with A and inclining towards D, to facilitate the removal of condensed water.

The tubes C, are about  $\frac{1}{8}$  inch in diameter and are provided with cocks at E.

When distillations are in operation the brass tubes C are connected with glass tubes by means of rubber tubing; the glass



tubes reach nearly to the bottom of the distilling flasks and are provided with ground glass stop-cocks at F. D carries off the condensed water from B.

The entire apparatus is suspended from the ceiling by stiff iron rods. The condensers are arranged at right angles to, and immediately underneath B. The table is provided with both cold water and waste pipes for the condensers.

B must be high enough to permit the use of Bunsen burners under the distilling flasks.

Before starting distillations, all of the cocks E, must be opened and steam turned on, to blow out condensed steam; they are then closed, the distilling flasks connected as described above

<sup>1</sup> Read December 8, 1893.



and the cocks E again opened, taking care to have the ground glass cocks F closed.

During distillation the steam is controlled by the stop-cocks F, and the operation is further regulated by the use of Bunsen burners under the distilling flasks. One person can easily attend to six or more distillations at one time.

Experience of more than a year has proved the utility of this arrangement, where many samples involving analysis by distillation, have been presented in a day.

### A NEW MUFFLE FOR INCINERATION OF SUGAR.<sup>1</sup>

BY H. SCHWEITZER AND E. LUNGWITZ.

THE incineration of sugar for the determination of ash is generally carried out in platinum dishes which are placed in a muffle of platinum (Scheibler) or of Russian sheet iron (F. G. Wiechmann) kept at a dull red heat. The platinum muffles to hold two dishes, weigh from sixty to seventy-five grams, and are very expensive apparatus. Moreover it happens very often that in a platinum muffle the last portions of carbon are oxidized with difficulty. Frequently a little higher temperature under the muffle of platinum which is such an extremely good conductor of heat, causes the ash to fuse and the melted salts, including unburnt carbon, form black blotches in the dish. On account of the insufficient draught in the platinum muffle it is then very difficult to accomplish perfect incineration. In such a case, as Tucker says in his manual of sugar analysis, the dish is allowed to cool, one or two drops of sulphuric acid added, and the dish heated cautiously at first to avoid spattering and finally brought to redness for fifteen minutes. Naturally such proceeding causes delay and does not contribute to the exactness of the determination.

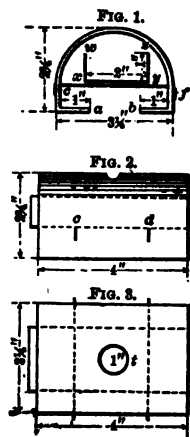
The muffles of iron are impracticable for quick commercial work because the incineration in them takes much longer time than in those of platinum.

These considerations prompted us to devise an apparatus, better fitted for the incineration of sugar than the muffles mentioned above.

<sup>1</sup> Read December 8, 1893.

The accompanying cuts show how we solved this problem.

A French clay muffle is cut open at the bottom; (see Fig. 1, *a, b*) through the walls of the muffle at both ends holes are bored (Fig. 2, *c, d*) through which platinum wires are fastened in the manner shown in Fig. 1, *c, f*. These wires serve as support for the bent platinum sheet, (Fig. 1, *w, x, y, z*) on which the dishes containing the sugar are placed. In the center of the top of the muffle a round hole is cut out, (Fig. 3, *t*). The bent sheet *w, x, y, z*, can also be made of Russian sheet iron. The muffle is placed on a tripod and heated as usual.



This construction produces a good draught in the muffle and allows the use of the largest flame of the so-called "Acme" burner which accelerates the incineration very considerably. Whereas the complete incineration under normal conditions in a platinum muffle lasts from about forty to forty-five minutes, it lasts only twenty-five to thirty minutes in our platinum clay muffle and about forty-five minutes in our platinum iron muffle. The short time in which our platinum clay muffle works, naturally reduces the expense for gas. For about one year we have had both kinds of clay muffles in constant use and always obtain light and flaky ash and never a fused ash.

We feel assured that these new muffles, saving time and money, will be welcome additions to the outfit of every sugar laboratory.

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## A FEW REMARKS ABOUT BASIC SULPHATE OF ALUMINA.<sup>1</sup>

BY W. C. FERGUSON.

**M**ANY samples of commercial sulphate of alumina contain more or less of an excess of alumina over that required to form the normal sulphate ( $\text{Al}_2(\text{SO}_4)_3$ ), the amount varying from a trace to  $2\frac{1}{2}$  per cent. and occasionally even more.

The following composition is of frequent occurrence:

Total soluble alumina = 17.00 per cent.; soluble alumina calculated from sulphuric anhydride ( $\text{SO}_3$ ) to form  $\text{Al}_2(\text{SO}_4)_3$  = 15.2 per cent., leaving 1.8 per cent. of alumina in excess of that required to form the normal sulphate.

It is concerning the probable chemical constitution of this alumina in excess of that required to form the normal sulphate, together with its behavior towards resin soap in the manufacture of paper, that this brief article is written.

As is well known, in sizing paper sulphate of alumina is made to react on resin soap (made by saturating soda ash with resin), thus precipitating an insoluble alumina soap, a resinate of alumina in the fiber of the paper.

In many paper works the per cent. of normal sulphate  $\text{Al}_2(\text{SO}_4)_3$ , determines the strength of the material bought and, other things being favorable, that is preferred which contains the highest per cent. of  $\text{Al}_2(\text{SO}_4)_3$ .

A number of reports from paper mills are about as follows:

{	Combined $\text{Al}_2\text{O}_3$ = 15.20 = $\text{Al}_2(\text{SO}_4)_3$ = 50.96
	{ Free $\text{Al}_2\text{O}_3$ = 1.80, or
{	$\text{Al}_2(\text{SO}_4)_3$ = 50.96
	{ $\text{Al}_2\text{O}_3$ = 1.80

In such reports the "combined"  $\text{Al}_2\text{O}_3$ , and also the  $\text{Al}_2(\text{SO}_4)_3$ , are calculated from the  $\text{SO}_3$  present and the soluble so-called "free"  $\text{Al}_2\text{O}_3$  is ignored as being of no value for sizing purposes. This idea that has so little, if anything, to support it, is discussed below.

A solution of normal sulphate of alumina behaves very much

<sup>1</sup> Read January 12, 1894.

like an acid; it combines with bases, evolves hydrogen with metals, and is acid to litmus paper. We should, therefore, expect  $\text{SO}_3$  to combine with more alumina than is represented by the normal sulphate, and it might be added that as weak bases have the characteristic of forming basic salts, we should for this reason also anticipate the formation of basic sulphates of alumina. These basic sulphates can readily be formed in the laboratory from the normal sulphate.

1. By dissolving alumina in the normal sulphate.

2. By action of caustic alkalies on a solution of the normal sulphate.  $\text{Al}_2(\text{SO}_4)_3 + \text{Na}_2\text{O} = \text{Al}_2\text{O}_3(\text{SO}_4)_2 + \text{Na}_2\text{SO}_4$ .

For example: A solution of normal sulphate of alumina containing seven per cent. of alumina can be made two per cent. basic by adding caustic soda slowly to a hot solution until a precipitate forms that does not dissolve even on long boiling. This is equivalent in a seventeen per cent. material to having 4.86 per cent. in excess of that required to form  $\text{Al}_2(\text{SO}_4)_3$ .

3. By action of a metal,  $\text{Al}_2(\text{SO}_4)_3 + \text{Zn} + \text{H}_2\text{O} = \text{ZnSO}_4 + \text{Al}_2\text{O}_3(\text{SO}_4)_2 + \text{H}_2$ .

These equations are only intended to illustrate the probable types of reaction; it is not assumed that just such compounds are formed.

The following standard works treat of a number of basic sulphates of alumina that are soluble in water:

"Watts' Dictionary of Chemistry,"

"Roscoe & Schorlemmer's Chemistry,"

"Mendelejeff's Principles of Chemistry."

A careful search through the literature fails to reveal any reference to "free" alumina existing in a solution of normal sulphate.

The term "free" implies the reverse of combined and from the considerations given above it is not deemed best to call the alumina contents in excess of that required to form normal sulphate "free," with every condition favoring combination. Such alumina is undoubtedly combined as basic sulphate and being in solution there is every reason to believe that it would form a resinate of alumina with resin soap as readily as the normal sulphate, and some ground for the assumption that it might be even more available because it is probably held in weaker combination

and so would be more readily decomposed and precipitated as size; and if this were true such basic alumina would be more valuable than the normal because more would be precipitated by a given weight of resin soap. With these considerations in mind the following investigations were carried out in the laboratory. In order to observe the action of resin soap on a solution in which the alumina approaches nearest to the free state some aluminate of soda was prepared by dissolving alumina in caustic soda. In this solution alumina is so feebly held in combination that the weakest acids, such as carbonic, will replace it. The solution is basic, and alkaline to test paper.

Resin soap immediately precipitates a voluminous precipitate of resinate of alumina. Even upon the addition of a drop or two of resin soap the precipitate begins to form.

A comparison of a neutral sulphate containing seventeen per cent. soluble alumina and of a basic sulphate containing seventeen per cent. total soluble alumina, fifteen per cent. being normal and two per cent. being basic, the so-called "free," were each treated with an equal amount of resin soap in such quantity that but a portion of the alumina was precipitated. The solutions were filtered and precipitates washed with equal amounts of water and ignited. It was found that under such conditions

4.40 grams were precipitated from the neutral solution,

6.98 grams were precipitated from the basic solution.

These results are what theory would anticipate.

A brief summary of the case is this: It would seem that there is no "free" soluble alumina in the basic sulphate of alumina of commerce; such alumina is in direct combination as basic sulphate and being more feebly held in combination than alumina combined as normal sulphate, more readily forms size with resin soap and is therefore more economical, less resin soap being required for a given weight of sulphate. It directly follows from this that in any sulphate of alumina the  $Al_2(SO_4)_3$  should be calculated from the total soluble alumina and *not* from that combined as normal sulphate alone, as in the latter case the most valuable alumina content is ignored as being useless. The following example will serve to illustrate the difference in value based on the two types of analyses: In a sulphate of alumina analyzing

Total soluble alumina.....	17.00 per cent.
Alumina combined as normal.....	15.20 " "
Basic alumina = so-called "free" .....	1.80 " "

The  $\text{Al}_2(\text{SO}_4)_3$ , calculated from 15.20 per cent. of alumina equals 50.96 per cent., whereas if calculated from 17.00 per cent. the  $\text{Al}_2(\text{SO}_4)_3$ , equals 57.00 per cent. In conjunction with these figures it must be borne in mind that experiment proves the basic sulphate of alumina to be relatively even more efficient than the difference in the above interpretations of analysis indicate.

### DROPPING FLASK FOR STANDARD SOLUTIONS.<sup>1</sup>

BY FRANK VANDERPOEL.

IT is well known that in working with standard solutions, the strength of the latter, when determined by the volume used, is influenced by the temperature to quite an appreciable extent. In fact, if a solution be standardized at 25° C. and afterward used at 20° C., its strength at the latter temperature is 1.001 times what it was at the former. For this reason it is necessary when employing volumetric apparatus to note the temperature of the solutions if very accurate work be done.

Again it has been observed that burettes and delivery pipettes sometimes vary in the volume of liquid delivered, this variation depending upon the nature of the solution or the ease with which it wets the sides of the glass tube, as all solutions are not the same in this respect.

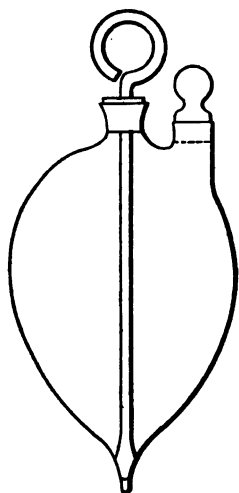
With an apparatus so made, however, that the standard solution is weighed instead of measured, these objections disappear, while accuracy is not impaired; in fact, with a common balance, sensitive to one centigram, much finer work can be done by weighing the solution than by measuring with a burette which reads to tenths of a cubic centimeter.

A number of dropping flasks and bottles have been invented from time to time with the above object in view; the one here represented having been devised some four or five years ago and kept in constant use in my laboratory ever since. It is quite simple and consists of a cylindrical or globular flask provided with two openings at the top and a dropping tube at the bottom

<sup>1</sup> Read December 8, 1893.

into which a glass rod is ground so as to make a tight joint. The rod runs through a perforated stopper in the central opening at the top in order that it may be kept in proper position. The second opening at the top is used when it is necessary to fill the bottle.

The apparatus may be supported by a small light tripod upon the pan of the balance, or it may be provided with two small hooks of brass wire fastened to a collar of the same metal which encircles the upper central tubulus. By means of these hooks the bottle is easily and quickly suspended from the bows supporting the balance pans.



I make use of a common pulp scale with four inch pans, and after counterpoising the filled bottle by means of brass cup weights supplemented by fine shot, perform the titration, and upon its completion determine the amount of liquid used by adding weights to that side of the balance from which the bottle is suspended. This necessitates but one calculation. The bottle

may be used for solution of potassium permanganate or silver nitrate or in fact any solution which is generally employed in a burette furnished with a glass stop-cock.

It is very readily taken apart, cleaned and dried.

NEWARK, N. J.

## ON THE ESTIMATION OF POTASSIUM IODIDE AND SODIUM ACETATE IN THE PRESENCE OF COMPLEX ORGANIC MIXTURES.<sup>1</sup>

BY JAMES H. STEBBINS, JR., PH.D.

I RECEIVED a short time since a sample of medicine for examination, which on qualitative analysis was found to contain potassium iodide and sodium acetate, together with certain complex vegetable extracts, and as the determination of the first two named compounds gave me a great deal of trouble before a

<sup>1</sup> Read January 19, 1894.

satisfactory method of analysis was found, I thought that an account of the process finally adopted, though containing no great novelty, might be of assistance to some of my colleagues should they ever by chance have to examine a mixture of this kind.

*Potassium Iodide.*—This compound was determined as follows without any trouble:

Ten cc. of medicine were diluted with 100 cc. of distilled water, and the salmon colored flocculent precipitate formed collected upon a filter.

After thoroughly washing the filter out with cold water, the iodine in the filtrate was determined as usual as iodide of silver and then calculated to iodide of potassium. The amount of the latter compound found was 3.58 per cent.

*Sodium Acetate.*—It was first sought to determine the acetic acid in the mixture as such in the usual way, by distillation with sulphuric acid, and from the quantity so found to calculate the percentage of sodium acetate present, but it soon became evident that this process could not be used, as the sulphuric acid was found to liberate iodine as well as acetic acid whose estimation was thus rendered impossible.

It was next sought to arrive at the percentage of sodium acetate by an examination of the ash left after igniting the dry extract. But unfortunately the usual method of incineration was found to be of no avail, as by this process the sodium acetate is either wholly or partially converted into sodium carbonate, no uniform products being obtainable, and the potassium iodide is likewise subject to decomposition and volatilization. Moreover it was found impossible to obtain an ash absolutely free from carbon, it always being necessary to treat the ash after ignition with water to free it from a small carbonaceous residue and then to ignite this residue a second time, to add its ash to the aqueous solution, to evaporate the whole to dryness, and to determine the per cent. potassium and sodium present as sulphates by the well-known process of indirect analysis.

As, however, no satisfactory conclusions could be reached in this way the following method was finally adopted:

Ten cc. of fluid extract were pipetted off into a capacious platinum dish and mixed with thirty cc. of twenty per cent. sulphuric



acid. The contents of the dish was now evaporated upon a steam bath to the consistency of a thick syrup. The dish was then transferred to a sand bath and gently heated until the contents had charred and no more fumes of sulphuric acid or iodine were given off. A compact carbonaceous mass will thus be obtained, which contains all the sodium and potassium in the fluid extract as sulphates. The contents of the dish were now moistened with ammonium nitrate solution evaporated to dryness over the steam bath, and then ignited over the direct flame of a Bunsen burner.

The carbon will in this manner be completely consumed, leaving a perfectly white residue of sodium and potassium sulphates, which are then further examined by the process of indirect analysis.

In the present case the sum of the sulphates of potassium and sodium, from ten cc. of fluid extract, was 0.2499 gram.

The amount of  $\text{SO}_4$  contained in the 0.2499 gram of sulphates was 0.1208 gram, or equivalent to:

Sodium sulphate .....	0.57 per cent.
Potassium sulphate.....	1.92 " "

On now calculating the sodium sulphate to sodium acetate, and the potassium sulphate to potassium iodide, we get:

Sodium acetate.....	0.65 per cent.
Potassium iodide.....	3.65 " "

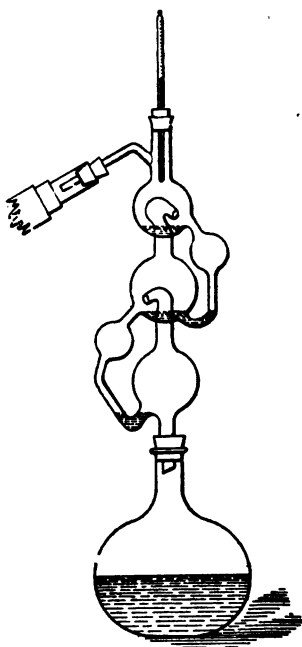
In the direct determination of the potassium iodide, as iodide of silver, we obtained 3.58 per cent. potassium iodide; hence it will be seen that the agreement between the direct and indirect methods of analysis is considering the complexity of the mixture under examination very satisfactory.

NEW YORK,  
NOVEMBER 19, 1893.

## APPARATUS FOR FRACTIONAL DISTILLATION<sup>1</sup>

By C. W. VOLNEY.

**T**HIS apparatus for fractional distillation of mixtures of liquids of different boiling points is constructed on the dephlegmator principle. Although the opening of the recurved main tube is never closed by the condensed liquid, comparatively only small quantities of vapors of the liquids, condensable in the respective bulbs, ascend or ultimately escape in the condenser, so that by a second distillation liquids of practically uniform boiling points are obtained.



I have used this apparatus for the preparation of paraffins and benzene derivatives, and can recommend it as a good and practical instrument. The principle employed is evident from the figure, and any glass blower can make it.

NEW YORK,  
NOVEMBER 23, 1893.

<sup>1</sup> Read December 8, 1893.



## THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(Continued from 15, 181, 1893.)

By THOMAS B. STILLMAN, PH.D.

N<sup>O</sup> standard specifications for the testing of Portland cement are required in Great Britain, the determination of fineness, tensile strength and variations in volume, being considered sufficient to determine the value of a cement. The machines for

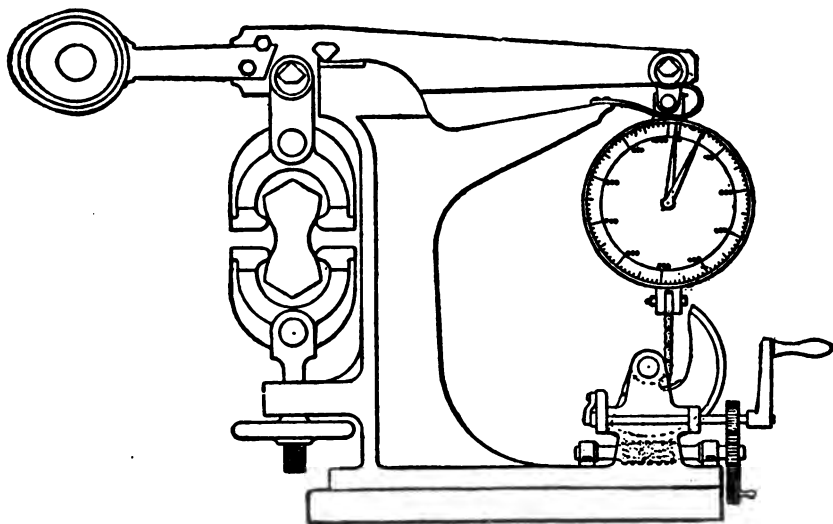


Fig. 5.

tensile strength are the "Faija" (Fig. 5), the "Reid and Bailey" (Figs. 6 and 6a), or the "Grant," the latter described in *Proceedings* of the Institution of Civil Engineers, **62**, 113. The "Reid and Bailey" is essentially the "Michaelis" (Fig. 4), excepting that water is used instead of fine shot for the breaking power.

It is readily seen that the "Faija" and "Grant" machines, not being automatic, require the application of the power at a certain uniform speed to obtain comparable results, since a difference of twenty-five per cent. in tensile strength may be obtained by applying the strain very quickly or very slowly (*Proceedings* of the Institution of Civil Engineers, **75**, 225, 226).



Fig. 6.

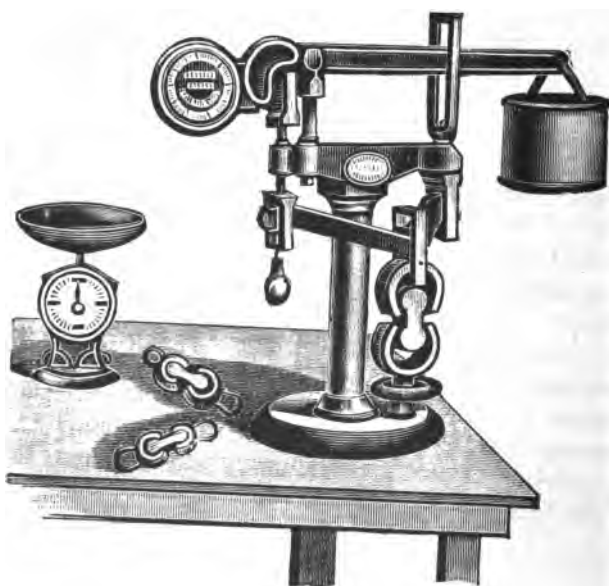


Fig. 6a.

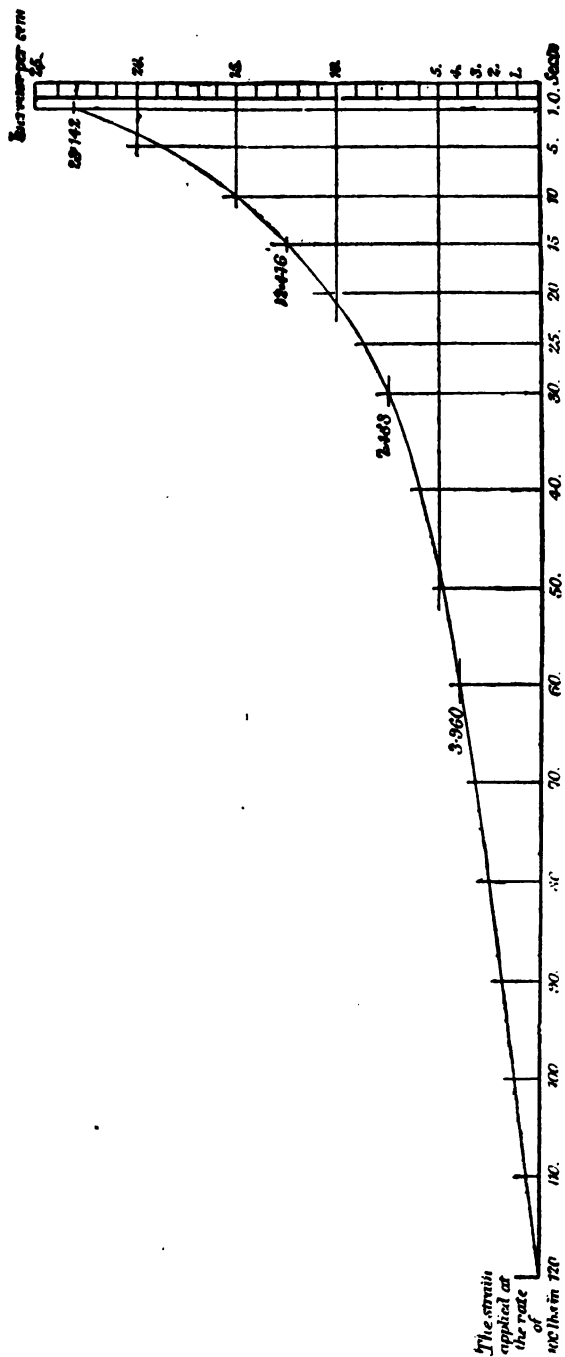


Fig. 7.

Faija has determined this variation with extreme care, the result being indicated in the curve shown in Fig. 7. To overcome these variations a uniform speed of 400 pounds per minute has been accepted as the standard.

Not only are comparable methods required in the use of the machines to obtain uniform results, but the briquettes must also be constructed under similar conditions.

It is manifestly unjust to compare the tensile strength of two cements (even when the briquettes are broken upon the same machine) unless the briquettes have the same weight of water for mixing; the same pressure with the trowel when being formed in the molds, and the same length of time of exposure under water before submitting the briquettes to the tensile strain. Usually the greatest difference is due to the pressure exerted in forming the briquettes.

For instance: Comparing tests made upon the Dyckerhoff Portland cement by Dr. Böhme, Director of the Royal Commission for testing building materials, at Berlin, and by E. J. De Smedt, General Inspector Engineer Department, District of Columbia, we find that the German method gives a much higher tensile strength than the method in use in this country.

DR. BÖHME.		
Age of Briquettes.	Average tensile strength per square inch.	Number of tests.
7 days.....	767 pounds	10
28 " .....	895 "	10
E. J. DE SMEDT, C. E.		
Age of briquettes.	Average tensile strength per square inch.	
5 days.....	250 pounds	
30 " .....	700 "	

Showing:

109 pounds increase per day (7 days), Dr. Böhme,  
50 " " " " (5 days), De Smedt,

or over 100 per cent. difference upon the same cement.

These variations are undoubtedly due principally to the different pressures upon the cement during the making of the briquettes, and to overcome difficulties of this nature the Vereins deutsche Portland Cement Fabrikanten have modified the rules in the construction of the briquettes so that two methods are acceptable:

First. The normal method, above given, with the trowel, etc., ("Handarbeit").

Second. The use of the Böhme-Hammer apparatus or "machine method," by which the cement in the briquette form

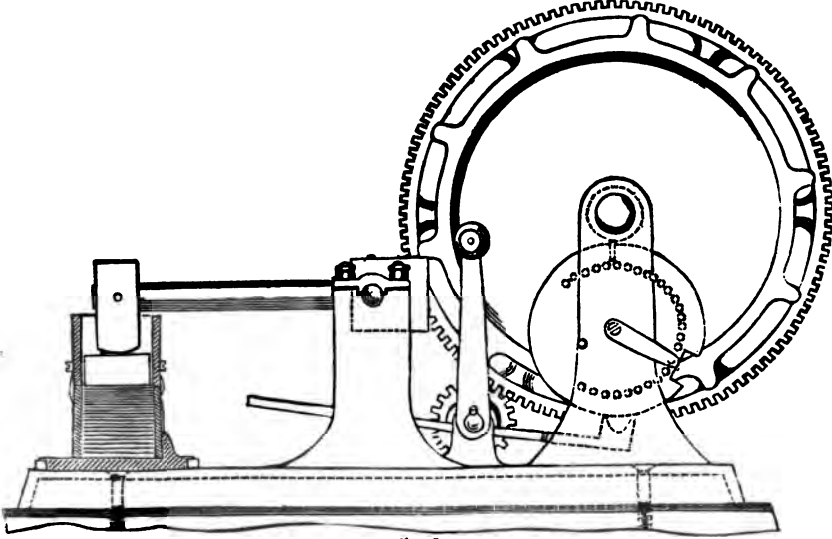


Fig. 8.

(after mixing with proper amount of water), is submitted to a pressure of 150 blows from a hammer weighing two kilos (Fig. 8). The briquette of cement is then removed from the mold and treated for tensile strength as usual.

This subject is receiving considerable attention at the present moment, the evident purpose being to render the tests of tensile strength as uniform as possible by making the working of the apparatus automatic and the production of cement briquettes with the least possible variation in the pressure in the molds.

In this case, no matter how careful the experimenter may be, the "personal equation" enters largely into the results of testing hand-made briquettes, for which reason the manufacture of the briquettes should be as automatic as possible. In no other way can results obtained by different experimenters be compared.

Prof. Charles D. Jameson describes an apparatus for this purpose (Fig. 9). *Transactions of the American Society of Civil Engineers*, 25, 302.

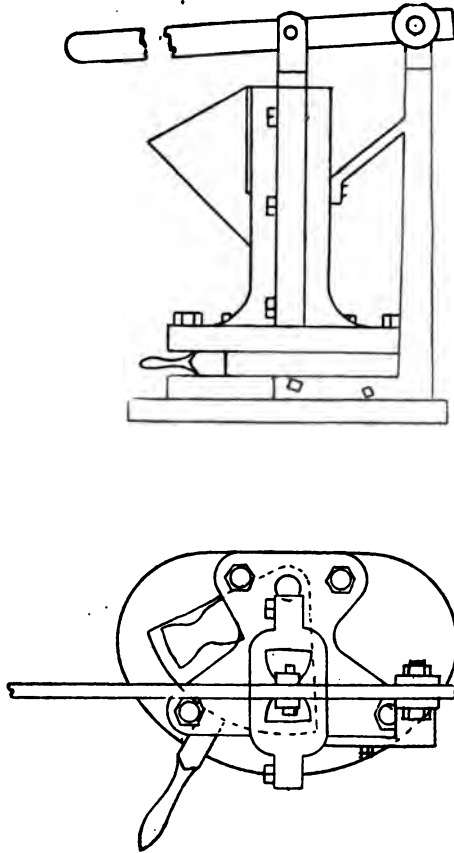


Fig. 9.

The method of operating is as follows: The lever being raised so that the lower end of the piston or main plunger is above the hole in the side of the cylinder communicating with the hopper, cement is put in the hopper and pushed down into the cylinder. The molding plate is pushed against one of the stops, so that one of the openings is beneath the bore of the cylinder. The long lever is forced down, causing the



plunger to force the cement into the opening in the molding plate. After this, the molding plate is swung against the other stop, cutting off the briquette, placing it over the plungers, throwing the other opening in the molding plate directly beneath the cylinder. The smaller lever is lifted, raising the plunger, and forces the briquette out of the mold, after which it is removed. The plunger is then pressed down, the main lever also, the molding plate swung back to the first position, the other plunger lever lifted, and another briquette is ready to be taken away, and so on. After making three briquettes, the main lever is lifted and more cement placed in the cylinder. The machine is best operated by two men, one to feed and operate the long lever, and the other to swing the molding plate, remove the briquettes, and lower the plungers. The pressure on the briquette is 175 pounds per square inch.

The conditions required in France for a good cement are:<sup>1</sup>

First. Analysis to determine the chemical composition.

Second. The determination of density.

Third. The determination of fineness.

Fourth. The determination of tensile strength.

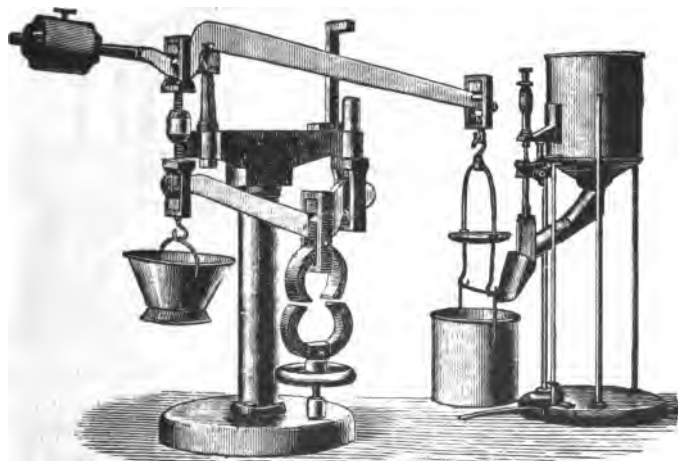


Fig. 10.

Fifth. The determination of crushing strength.

<sup>1</sup> E. Caudlot, *Ciments et Chaux Hydrauliques*, Paris, Baudry and Co., 1891.

Sixth. The determination of variations in volume.

The tensile strength is determined by the use of a Michaelis machine, Fig. 10, or the use of a Buignet apparatus, Fig. 11, this latter being upon an entirely different principle than any yet in use, and is thus described by the designer, M. Buignet, Conductor des ponts et chaussées au Havre :

It is composed of a basin A and frame B.

The basin A, filled with mercury and water, closes up by a diaphragm of rubber covered with a metallic disk, and is in direct communication with :

(a) Manometrique tube D.

(b) With a movable reservoir R, filled with mercury, by means of a rubber tube T.

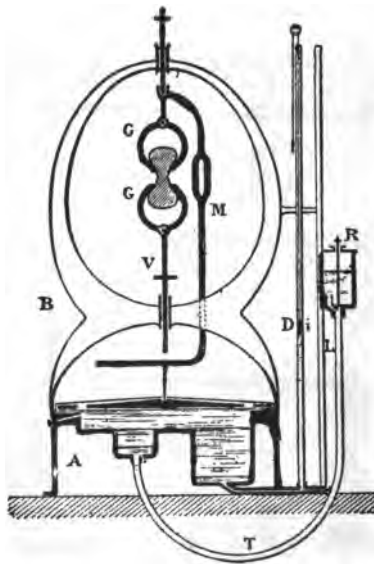


Fig. 11.

The grips G G, in which are to be placed the briquettes to be tested, are fastened, one to the frame B by the support V, the other to the support M, which rests upon the center of the metallic disk over A. It is operated as follows : The briquettes are placed in the grips G G, and the support V moved up or

down until equipoise is established, and then firmly secured by a crank in frame B.

The support M is adjusted until the point at its lower end just touches the metallic disk in A.

By gradually lowering the reservoir R an upward pressure is given to the metallic disk in A, which is transferred to the support M, until when sufficient pressure is exerted the briquette is broken. The moment rupture of the briquette, takes place, the pressure required to do this is indicated by the float *i* in the manometer tube D.

Another instrument made use of to determine tensile strength, and used at l' ecole des ponts et chaussées, Paris, is shown in Fig. 12.

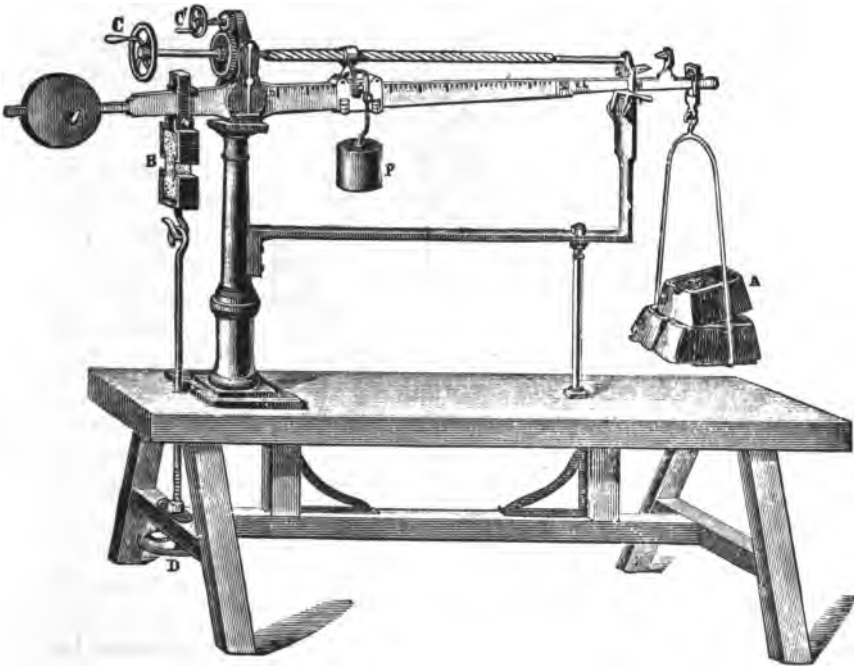


Fig. 12.

It is similar in principle to the Riehle machine (Fig. 2), and the Grant machine (*Proceedings of the Institution of Civil Engineers*, 62, 98).

By a comparison of the various machines used in Germany, England, France, and the United States, we find practically but two in general use. The "Michaelis" (Figs. 4, 10, and 11), and the "Grant" (Figs. 2 and 12). While nearly all engineers require cements to be subjected to the tensile strength test, in fact relying more upon this one test than any of the others, it might be well to include here the opinion of H. Le Chatelier, professor at the École des Mines, Paris, France, as given in a paper presented at the last meeting of the American Institute of Mining Engineers, August, 1893, entitled "Tests of Hydraulic Materials," p. 44.

"The method of tension is at present most widely used, but the preference for it is not well founded.

"Here, as in rupture by bending, only the *surface* of the briquettes acts in a really useful way, and its inevitable irregularities and alterations so greatly affect the precision of the results that they can in no case be trusted nearer than about twenty per cent.

"This preponderant influence of the superficial parts was first shown by the fact that the resistance of briquettes of different sizes increases, not with the section, but, on the contrary, with the perimeter. Finally, M. Durand-Claye has shown that the interior of a briquette may be removed without notably diminishing its resistance to rupture by tension, and has given a complete theoretical explanation of the phenomena which seemed at first sight paradoxical."

#### THE CRUSHING TEST.

This test is not official in this country and is seldom required by our engineers, who, however, have confined their experiments in this direction mainly to crushing tests of concrete, formed by mixing Portland cement, sand, and broken stone.

Tests upon cubes of neat cement and of mortar composed of one part cement and three of standard sand, are generally included in reports given upon the examination of cements in Europe, the ratio being that the crushing strength is about ten times greater than the tensile strength.

Thus, a cement of good quality should show the following resistances per square centimeter:

## TENSILE STRENGTH.

	7 days.	28 days.
Neat cement .....	25 kilos	35 kilos
1 part cement } .....	10 "	18 "
3 parts sand }		

## CRUSHING STRENGTH.

	7 days.	28 days.
Neat cement .....	250 kilos	350 kilos
1 part cement } .....	100 "	180 "
3 parts sand }		

To convert kilos per square centimeter to pounds per square inch, the equivalents used are: one kilo = 2.204 pounds English; 6.451 square centimeters = one square inch English.

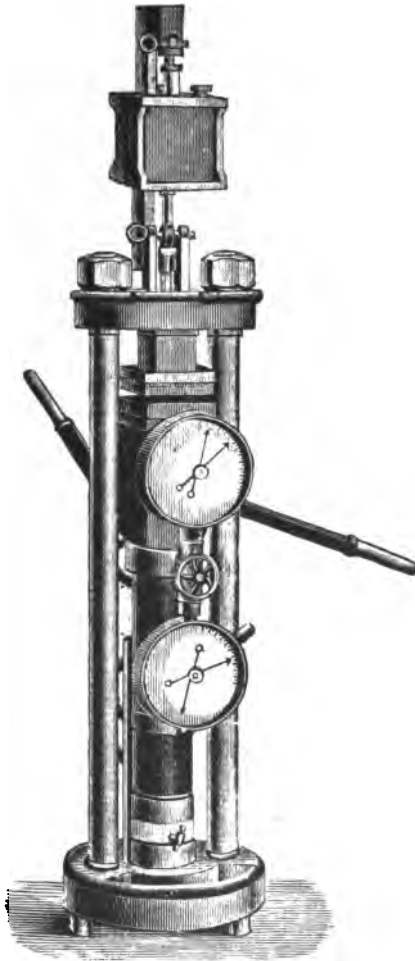


Fig. 14.

The hydraulic presses made use of for this purpose, a few years since, gave very discordant results, as it was impossible to distribute the pressure evenly over the surface of the cubes. This has been overcome, and there are now four machines upon the market whose results are comparable, *viz.* :

The "Suchier," Fig. 14; the "Böhme," Fig. 15; the "Tetmajer," as improved by Prof. Amsler-Laffon,<sup>1</sup> and the "Brink and Hubner."<sup>2</sup>

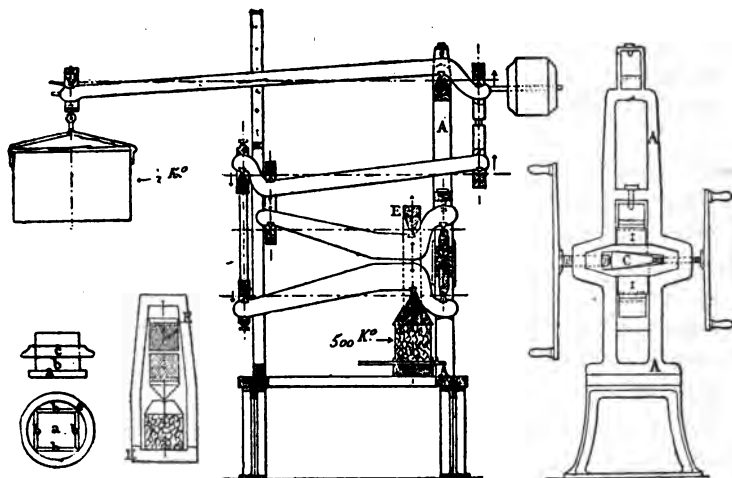


Fig. 15.

*Variation in volume* (expansion or contraction).—The method of Faija<sup>3</sup> the one generally used for this purpose is as follows :

Three pats should be made on pieces of glass or other non-porous substance, and their behavior watched under the following conditions :

Pat No. 1 may be left in the air, and No. 2 should be put in water as soon as it is set hard.

Pat No. 3 should be treated in the apparatus for determining

<sup>1</sup> Consult: *Schweizer Bauzeit*, January 12, 1889.

<sup>2</sup> Description of the "Suchier," "Böhme," and "Brink and Hubner" machines will be found in *Der Portland Cement und seine Anwendungen im Bauwesen*, Berlin, 1892.

<sup>3</sup> The determination of liability to "checking" or "cracking" (variation in volume) in Portland cements as recommended by *American Society Civil Engineers*, is not as complete as Faija's method, see this JOURNAL, 15, 184.

the soundness of cement. The apparatus consists of a covered vessel in which water is maintained at an even temperature of  $110^{\circ}\text{C}$ ; the space above the water is therefore filled with the vapor rising therefrom, and is at a temperature of about  $100^{\circ}\text{C}$ . Immediately the pat is gauged, it should be placed on a rack in the upper part of the vessel, and in five or six hours it may be placed in the warm water and left therein for nineteen or twenty hours. If, at the end of that period, the pat is still fast to the glass and shows no signs of blowing, the cement may be considered perfectly sound; should, however, any signs of blowing appear, the cement should be laid out in a thin layer for a day or two, and a second pat made and treated in the same manner, as the blowing tendency may only be due to the extreme newness of the cement.

If pat No. 3 shows the cement to be unsound, pats No. 1 and 2 will eventually prove it, but it may be weeks or even months before they develop the characteristics. If pat No. 2 blows, it may be because it was put in the water before it was set. A cement is considered set hard when it can no longer be marked by the pressure of the thumb nail.

*Résumé:*

The determination of the value of Portland cement therefore requires the following tests:

First. Chemical analysis.

Second. Determination of fineness.

Third. Determination of tensile strength, including the use of automatic briquette machines as well as an apparatus for mixing the cement with water, as "Faija" mixing machine.

Fourth. Determination of crushing strength.

Fifth. Determination of variation of volume.

## RECENT PROGRESS IN THE ANALYSIS OF CATTLE FOODS.<sup>1</sup>

BY F. W. WOLL.

OUR methods of analysis of cattle foods are essentially the Weende methods, published nearly thirty years ago in *Landw. Versuchs Stationen*, 6, (1864,) 496, by Henneberg. An outline of the methods as given in the place cited, will at once show this to be true.

Henneberg gives the following directions for the determination of the various components of fodders.

1. *Water*.—A few grams of the finely powdered, air-dry sample are heated at 100–110° C., and the results calculated on the original substance.

2. *Mineral Matters* (ash excluding carbon dioxide).—100 to 200 grams are ignited in a muffle oven at as low temperature as possible, and the crude ash weighed, carbon dioxide and char are then determined in a portion of the crude ash, and corrections made accordingly.

3. *Protein*.—Determination of nitrogen and using the factor 6.25.

4. *Crude Fiber*.—A quantity corresponding to three grams water-free substance is taken, and heated for one-half hour in a flat porcelain dish with 200 cc. of a 1½ per cent. sulphuric acid solution, adding water as it boils away; the solution is then left to settle and the clear liquid pipetted off into a beaker; the sample is again boiled for one-half hour with water, the clear liquid pipetted off into the same beaker as before, and the operations of boiling with 200 cc. of water and pipetting off repeated a second time. 200 cc. of a 1½ per cent. potassium hydroxide solution are then added and boiled for half an hour, the clear liquid pipetted off into a second beaker, the residue boiled twice with 200 cc. of water, each time uniting the liquid with that already in the second beaker. The residue is then brought on a filter and also that which has settled in the beaker containing the alkaline fluid; the filter is washed until neutral reaction, when the residue in the other beaker is added and the washing repeated and finished by

<sup>1</sup> Read before the World's Congress of Chemists, August 24, 1893.



successive washings with alcohol and ether, drying, weighing, and incineration, which gives the crude fiber by difference.

5. *Ether Extract* (fat).—Complete extraction with boiling anhydrous ether, distillation of the united filtered distillates, and drying the residue at 100–110° C.

Since these methods were first published, our knowledge of the composition of plants and feeding stuffs has been greatly widened; we understand far better than did the writers thirty years ago, what the various groups separated out by the Weende experimenters include, and the conditions which must be observed in each case in order to obtain correct results. But on the purely analytical side we have made but very little progress; the problems have grown more complex every year, and the difficulties of the problems have increased much faster than has our ability to meet them.

In giving a short account of the progress made during recent years in the analysis of cattle foods, I shall take up the various components in the order adopted by Henneberg and still followed by agricultural chemists in general, and shall show the changes which the methods have undergone and suggest the reason for these changes.

As shown by Wilm, Bahring, Baessler, and others, *moisture* cannot be determined in many of our food stuffs by a simple drying in the air, as the fat contained in them will oxidize and the sample thus increase in weight, which means a too low percentage of moisture. Desiccation must, therefore, be conducted in the medium of an indifferent gas; the gas now generally adopted for drying is hydrogen or carbon dioxide, preferably the former. Märcker has further shown that drying above 100° C. may cause formation of resinous substances, and Jenkins found that a volatile oily matter passed off when fodders were heated at 110° in the air or in other gases; the same was observed by Baessler, Wiley, and Cutter. The temperature ought, therefore, never to exceed 100° C. The time necessary for drying will depend on the kind of apparatus used and will vary from four to ten hours; in case of a dry current of hydrogen being passed through the samples, four to six hours will as a rule be found necessary, the velocity of the current being the deciding factor

as to the time required; 90 to 100 bubbles of hydrogen per minute is a maximum velocity (Anderson). The loss of volatile substances will be increased when a very rapid current is passed through the sample. Where the fodders are heated on watch glasses or in open disks in an atmosphere of hydrogen, longer time will be necessary than otherwise, sometimes as much as ten hours, the temperature of drying being all the time that of boiling water.

*Ether Extract.*—The determination of ether extract has been greatly facilitated by the adoption of the Soxhlet continuous extraction apparatus; the form of extraction tube generally used in the United States is the Johnson extractor, the most recent modification of this being the Caldwell extractor.

The ether extract is determined in the water-free sample, as the air-dry sample extracted with ether will give too high results, for obvious reasons. The ether to be used for extraction must be anhydrous and alcohol-free, as too high results will otherwise be obtained. Numerous comparisons of extraction with ether of different kinds and under varying conditions of drying previous to extraction, have been made by Atwater, Babcock, Wilm, Bahring, Wagner, Märcker and scores of others, and the above points have been fully settled.

As there are several reasons for believing that prolonged drying of any food stuff even at 100° C. modifies the solubility of the fat and the amount of ether extract found, the writer has recently proposed the use of anhydrous copper sulphate in ether extraction. The sulphate will dehydrate both fodder and ether used; and no special precautions for dehydration of either are necessary. The sample of 2-3 grams weighed out may be mixed with about five grams of copper sulphate and the mixture placed in the extraction tube and extracted as usual.

Stellwaag's and Maxwell's investigations have shown the complexity of the bodies making up the ether extract of most feed stuffs. The former found from 0.5 to 34.6 per cent. of insaponifiable components in twenty-five common fodders; lecithin, cholesterin, and hydrocarbons have been shown to be present in many cases, as well as coloring matters. It is especially the ether extracts of coarse fodders and roots which contain large pro-

portions of non-glycerides; the extracts of seeds of all kinds are as a rule fairly pure. Various methods have been proposed for the purification of the crude fat, but none have been generally adopted. The purification by means of animal charcoal, proposed by G. Kühn, nearly twenty-five years ago, and proved inaccurate by König in 1871, and by Schulze in 1872, was brought forward again a few years ago by Patterson, who obtained correct results with it. By more recent, thorough investigations it has been shown, however, that animal charcoal will retain fat from ethereal solutions passing through it. There is considerable difference in this respect between different kinds of charcoal, making the method entirely unsatisfactory in quantitative analysis.

*Crude Protein* is determined by multiplying the per cent. of nitrogen found by the Kjeldahl method by 6.25. A great step in advance was made in the adoption of this method (pub. 1883) in agricultural laboratories, and also in the separation of crude protein into albuminoids and amides, according to Stutzer's copper hydrate method (pub. 1880). The Kjeldahl method has been modified by a large number of chemists, and also so as to include nitrate nitrogen; the latter modifications most adopted are those of Jodlbauer and Ulsch.

*Crude Fiber*.—The Weende method is still the one used by most agricultural chemists. Schulze's method (pub. 1866) and Hönig's (pub. 1891) have both been proved unreliable by several chemists; but on the other hand the investigations made have also proved conclusively that the Weende method gives too low results, contrary to the experience of Kühn and Kern. In comparative determinations the results by the Weende method have come lower in every case, being often only one-half or two-thirds of those found by the Schulze or Hönig method in case of our ordinary cattle foods. It cannot, therefore, be denied that we are still without a satisfactory method for the determination of cellulose or crude fiber in fodders, and use the Weende method only for want of something better.

*Ash* is determined in a small quantity of the fodder at the present time, not exceeding ten grams. The manner of procedure is otherwise as in the Weende method; or the sample is

carefully burned at a low red heat, the crude ash treated with water, filtered, the residue ignited to whiteness, united with the filtrate, which is then evaporated and the residue heated to low red heat. The reason for this method of proceeding is the easy volatilization of chlorides by direct heating of the ash above red heat, which is necessary to burn the carbon of the ash.

*Nitrogen-free Extract* is determined by difference, as directed by Henneberg. The errors of analysis incident to the determination of all other components, therefore, enter here and often make the results unsatisfactory. The heterogeneous character of the bodies coming in under this head makes it unfortunate to class all together. A great deal of study has been expended in separating and identifying the various constituents of the nitrogen-free extract of fodders. Pentosans, as galactose, arabinose, xylose were discovered in cattle foods some years ago by Tollens, Schulze and their assistants, and have been found in appreciable quantities in nearly all our common food stuffs. While no satisfactory quantitative method for their determination has yet been devised, the furfural reaction, worked out by Stone, Allen, and Wheeler, gives a very sharp qualitative test for them.

If determinations of sugar, starch, and possibly also pentosans, could be made in our cattle foods, the rest of the nitrogen-free extract could be classed as *undetermined* and would then include many bodies present in all fodders, the properties of which we yet know very little about, and whose nutritive value is perhaps inferior.

From this short sketch we readily see that more progress has been made in our knowledge of the composition of food stuffs, and in the identification of these constituents than in their estimation. While brought to a certain perfection as far as working details go, the analytical side is yet far behind, and no fully satisfactory system of fodder analysis can be worked out until we are able to classify nutrients more according to their physiological importance than is done in our present methods.

## REPORT OF COMMITTEE ON DETERMINATIONS OF ATOMIC WEIGHT, PUBLISHED DURING 1893.<sup>1</sup>

BY F. W. CLARKE.

*To the Members of the American Chemical Society:*

YOUR committee, appointed at the last annual meeting, respectfully submits the following report, showing the advances made in our knowledge of atomic weights during 1893. The year has been one of reasonable activity in this branch of investigation, and it is thought that all the work actually published within its limits is here summarized and recorded. One partial exception possibly may be made to this statement. Morley's work on oxygen, reported orally at the American Association meeting, and at the Chemical Congress in Chicago, is omitted, for only unofficial abstracts of it have yet appeared in print. That work is of such fundamental importance that it seems best to await its completion, rather than to do it possible injustice by fragmentary notices which might be inexact.

In the "Stas Memorial Lecture," by Professor Mallet,<sup>2</sup> will be found a remarkably full discussion of the theory or philosophy of atomic weight determinations, which should be carefully read by all students in this domain. Taking the life and work of Stas as text and example, Mallet considers the conditions necessary to the fruitful continuation of that work, and throws out many suggestions of great practical value. He particularly advocates the multiplication of interdependent data, in order that errors may be eliminated; and he also recommends the establishment of a special, endowed laboratory, in which a group of trained observers may co-operate towards the attainment of the best results.

The individual atomic weight determinations of 1893 are subjoined.

*Boron.*—W. Ramsay and Emily Aston<sup>3</sup> redetermine the atomic weight of boron by two distinct processes, one of them being entirely new. First, with many precautions, they estimate

<sup>1</sup> Read at the Baltimore meeting Dec. 28, 1893.

<sup>2</sup> *J. Chem. Soc.*, August, 1893.

<sup>3</sup> *J. Chem. Soc.*, 63, 207, February, 1893.

the percentage of water in crystallized borax,  $\text{Na}_2\text{B}_4\text{O}_{10} \cdot 10\text{H}_2\text{O}$ ; all weights being reduced to vacuum standards. The same reduction is also made in their other series, but as they carry out the weights to seven decimal places, the corrections applied go farther than is necessary. In the subjoined tables I give the nearest tenth milligram.

Wt. $\text{Na}_2\text{B}_4\text{O}_{10} \cdot 10\text{H}_2\text{O}$ .	Wt. $\text{Na}_2\text{B}_4\text{O}_{10}$ .	Per cent. $\text{H}_2\text{O}$ .	At. Wt. B.
10.3582	5.4784	47.1099	11.04
5.3440	2.8247	47.1433	10.97
4.9963	2.6379	47.2026	10.85
5.7000	3.0101	47.1912	10.87
5.3143	2.8066	47.1882	10.88
4.9972	2.6392	47.1865	10.885
5.2367	2.7675	47.1524	10.955

Mean atomic weight,  $B=10.921, \pm 0.010$ .

In the second series of experiments fused borax was distilled with hydrochloric acid and methyl alcohol, and the residual sodium chloride was weighed. Results as follows:

Wt. $\text{Na}_2\text{B}_4\text{O}_{10}$ .	Wt. NaCl.	At. Wt. B. <sup>1</sup>
4.7684	2.7598	11.015
5.2740	3.0578	10.925
3.2344	1.8727	10.992
4.0862	2.3713	10.879
3.4970	2.0266	10.949

Mean atomic weight,  $B=10.952, \pm 0.010$ .

The distillations were conducted in soft glass flasks of about 100 cc. capacity, in which the sodium chloride was dried at about  $350^\circ$ , and finally weighed. It was found, however, that the flasks were somewhat attacked during the process, with liberation of silica, consequently some oxygen in the alkali of the glass had been replaced by chlorine, and the weight of the vessel increased. Another set of distillations was, therefore, made with flasks of hard combustion tubing, and these were slightly attacked also.

Wt. $\text{Na}_2\text{B}_4\text{O}_{10}$ .	Wt. NaCl.	At. Wt. B.
5.3118	3.0761	10.983
4.7806	2.7700	10.955
4.9907	2.8930	10.936
4.7231	2.7360	10.968
3.3138	1.9187	10.992

Mean atomic weight,  $B=10.966, \pm 0.005$ .

<sup>1</sup> Atomic weights used in Ramsay and Aston's calculations:  $\text{O}=16$ ,  $\text{H}=1.008$ ,  $\text{Ag}=107.92$ ,  $\text{Na}=23.05$ ,  $\text{Cl}=35.45$ , and  $\text{Br}=79.95$ .

As a check upon these results the sodium chloride was dissolved in water, and after filtration precipitated with silver nitrate. The resulting silver chloride was collected on a Gooch filter, dried at 200°, and weighed.

Wt. AgCl.	Per cent. Cl in NaCl.	At. Wt. B. from Cl.
7.5259	60.493	11.071
6.7794	60.515	11.024
7.0801	60.516	11.003
6.6960	60.514	11.039
4.6931	60.479	11.091

Mean atomic weight,  $B=11.052, \pm 0.010$ .

From all these results, and after discussing the supposable sources of error in them, the authors conclude that the atomic weight of boron is very nearly eleven.

Still another determination of the atomic weight of boron, by an entirely independent method, is due to Rimbach.<sup>1</sup> Taking advantage of the fact that methyl orange, as an indicator, is unaffected by free boric acid, he titrated solutions of borax with standardized hydrochloric acid, thus measuring the amount of sodium in the salt and thence calculating the value to be ascertained. The borax was prepared in platinum vessels from carefully purified boric acid and sodium carbonate; and the hydrochloric acid used contained 1.84983 per cent. of absolute HCl, determined gravimetrically as silver chloride. In the following table of results the titrated hydrochloric acid is given by weight in grams:

Wt. borax.	Wt. HCl. sol.	Per cent. Na. <sup>2</sup>	At. Wt. B. <sup>2</sup>
10.00214	103.1951	12.07081	10.9646
15.32772	158.1503	12.07138	10.9598
15.08870	155.7271	12.07530	10.9273
10.12930	104.5448	12.07517	10.9298
5.25732	54.2571	12.07435	10.9361
15.04324	155.2307	12.07283	10.9486
15.04761	155.2959	12.07448	10.9356
10.43409	107.6602	12.07176	10.9571
5.04713	52.0897	12.07480	10.9330

Calculating from the sum of all the weights the atomic weight of boron becomes 10.945,  $\pm 0.003$ .

<sup>1</sup> *Ber. d chem. Ges.*, 26, 164, February, 13, 1893.

<sup>2</sup> Calculations made with O=16, H=1.0032 (Keiser), Na=23.0575, Cl=35.4529, and Ag=107.9376.

**Carbon.**—Leduc<sup>1</sup> has determined the density of carbon monoxide, deducing thence the atomic weight of carbon. The globe used held 2.9440 of air. Filled with carbon monoxide the latter weighed

2.8470  
2.8468  
2.8469

Mean, 2.8469

Hence the density of CO is 0.96702, when air = 1, and with

O = 15.88,

C = 11.913,

If O = 16, then C = 12.003.

In a very brief note<sup>2</sup> Wanklyn announces that he has studied a series of hydrocarbons in which the successive steps rise—not by  $\text{CH}_2=14$ —but by  $\frac{1}{2}(\text{CH}_4)=7$ . If these observations are sustained, then the atomic weight of carbon becomes = 6.

**Cobalt and Nickel.**—Atomic weights determined by Winkler,<sup>3</sup> who starts with weighed quantities of metal, electrolytically deposited. This is then dissolved in a platinum dish in pure hydrochloric acid, and the chlorides produced are finally dried for several hours at 150°. In one set of experiments the chlorine in the chlorides is weighed gravimetrically, as silver chloride; in another set it is titrated with a standard solution of silver. In the first case we have the ratio R:2AgCl, in the other, R:Ag. Results as follows, for nickel:

Wt. Ni.	Wt. AgCl. (grav.)	At. Wt. Ni.
0.3011	1.4621	58.9102
0.2242	1.0881	58.9418
0.5166	2.5108	58.8571
0.4879	2.3679	58.9419
0.3827	1.8577	58.9304
0.3603	1.7517	58.8334
Mean result, Ni = 58.9033.		
Wt. Ni.	Wt. Ag. (vol.)	At. Wt. Ni.
0.1812	0.6621260	58.9253
0.1662	0.6079206	58.8665
0.2129	0.7775252	58.9584
0.2232	0.8162108	58.8811
0.5082	1.8556645	58.9684
0.1453	0.5315040	58.8631
Mean result, Ni = 58.9104.		

<sup>1</sup> *Compt. rend.*, 115, 1072.

<sup>2</sup> *Phil. Mag.*, (5) 36, 552, December, 1893.

<sup>3</sup> *Ztschr. anorg. Chem.*, 4, 10, 1893.



The following data were obtained for cobalt:

Wt. Co.	Wt. AgCl. (grav.)	At. Wt. Co.
0.3458	1.6596	59.6044
0.3776	1.8105	59.6609
0.4493	2.1521	59.7215
0.4488	2.1520	59.6577
0.2856	1.3683	59.7081
0.2648	1.2678	59.7480

Mean result, Co=59.6834.

Wt. Co.	Wt. Ag. (vol.)	At. Wt. Co.
0.177804	0.6418284	59.6495
0.263538	0.9514642	59.6396
0.245124	0.8855780	59.5996
0.190476	0.6866321	59.7311
0.266706	0.9629146	59.6388
0.263538	0.9503558	59.7092

Mean result, Co=59.6613.<sup>1</sup>

In the case of the cobalt determinations it is of course conceivable that the chloride formed might be contaminated with traces of basic compounds. This question is considered by Winkler in a supplementary communication.<sup>2</sup> The weighed, electrolytic cobalt, deposited upon the surface of a platinum dish, was treated with a solution of neutral silver sulphate. Silver was thrown down, and was washed, dried, ignited, and weighed. Thus a direct ratio was measured between silver and cobalt, involving no intervention of cobalt chloride, and consequently no error due to basic salts. Results as follows:

Wt. Co.	Wt. As.	At. Wt. Co.
0.2549	0.9187	59.7421
0.4069	1.4691	59.6377

The precipitated silver, as a check upon its purity, was dissolved in nitric acid, reprecipitated with hydrochloric acid as chloride, and filtered off. The filtrate, upon evaporation to dryness, gave traces of residue, containing cobalt. The amount of the latter in the first experiment was at most 0.5 milligram, and in the second not over 0.2 milligram. Correcting for these amounts the values found for the atomic weight of cobalt become 59.6356 and 59.6164, respectively. These figures fall within the limits of variation of those found in the first paper,

<sup>1</sup> All calculations with Ag=107.66 and Cl=35.37

<sup>2</sup> *Ztschr. anorg. Chem.*, 4, 462, 1893.

and show that the supposed error, if it existed, could not be large. The author admits, however, that the degree of concordance among his experiments is not so great as could be desired. The main purpose of his work was to show the essential constancy of the values, as opposed to the views of Krüss concerning the supposed composite nature of nickel and cobalt.

*Molybdenum*.—Atomic weight redetermined by Smith and Maas.<sup>1</sup> Sodium molybdate was converted into chloride by heating in a current of pure, dry, gaseous hydrochloric acid. Results as follows with weights reduced to vacuum standards:

Wt. $\text{Na}_2\text{MoO}_4$ .	Wt. NaCl.	At. Wt. Mo.
1.14726	0.65087	96.130
0.89920	0.51023	96.094
0.70534	0.40020	96.108
0.70793	0.40182	96.031
1.26347	0.71695	96.087
1.15217	0.65367	96.126
0.90199	0.51188	96.067
0.81692	0.46358	96.077
0.65098	0.36942	96.073
0.80563	0.45717	96.078

In mean, Mo=96.087.

*Palladium*.—Atomic weight determined by Joly and Leidié<sup>2</sup> by means of potassium palladio-chloride,  $\text{K}_2\text{PdCl}_6$ . In the first series of experiments the salt was dried in vacuo at ordinary temperature. It was then electrolyzed in a solution acidulated with hydrochloric acid, both the palladium and the potassium chloride being weighed. The palladium was dried, ignited in a stream of hydrogen, and cooled in an atmosphere of carbon dioxide. Results as follows:

Wt. salt.	Wt. Pd.	Wt. KCl.	From salt : Pd.	At. Wt. Pd.
1.0255	0.3919	0.5520	105.749	105.643
1.2178	0.3937	0.5551	104.881	105.535
1.2518	0.4048	0.5687	104.923	105.916

This series was rejected by the authors upon finding that the salt retained water. In one experiment 0.23 per cent. of water was found. Accordingly a second set of determinations was

<sup>1</sup> This JOURNAL, 15, 397, July, 1893. Results calculated with O=16, Na=23.05, and Cl=35.45.

<sup>2</sup> *Compt. rend.*, 116, 147, 1893. Results calculated with O=15.96, Cl=35.37, KCl=74.40, and H=1.

made in which the palladio-chloride was dried in vacuo at 100°

Wt. salt.	Wt. Pd.	Wt. KCl.	At. Wt. Pd.	
			Salt : Pd.	Pd : 2KCl.
1.3635	0.4422	0.6186	105.374	106.368
3.0628	0.9944	1.3929	105.545	106.229
1.4845	0.4816	0.6782	105.405	105.694
1.7995	0.5838	0.8206	105.427	105.861

The mean of the values found from the ratio  $K_2PdCl_4 : Pd$  is 105.438. If  $O=16$ , this becomes  $Pd=105.702$ . With  $O=15.88$  we get 104.910. The KCl values were rejected.

Still another set of determinations was based upon the reduction of the double chloride in a stream of hydrogen, the data being in other respects like the foregoing. Results as follows:

Wt. salt.	Wt. Pd.	Wt. KCl.	At. Wt. Pd.	
			Salt : Pd.	Pd : KCl
2.4481	0.7949	1.1168	105.560	105.911
1.8250	0.5930	0.8360	105.671	105.656

It is noticeable that these values, in the set  $K_2PdCl_4 : Pd$ , run higher than in the electrolytic series. Inasmuch as the latter experiments were made in presence of free hydrochloric acid, it would seem possible that chlorine may have been liberated, preventing complete precipitation of the palladium, and so slightly lowering the apparent atomic weight of the latter. At all events the results obtained are not sharply concordant, and are, therefore, inconclusive.

*Barium.*—An elaborate memoir upon the atomic weight of barium, by Richards,<sup>1</sup> makes a notable change in the value of that constant. Barium bromide was the compound investigated, and the procedure consisted in titrating its solution with solutions containing known quantities of silver. In many of the experiments the silver bromide thrown down during titration was collected and weighed. From the weights of Ag and of AgBr found, the ratio Ag:Br may be computed as a check on the accuracy of the work.

Full details are given concerning purity of materials, processes, weighings, etc., for which the original memoir must be consulted. The final results are stated in the following columns: First, BaBr, corresponding to 100 parts Ag. Second,

<sup>1</sup> *Proc. Amer. Acad.*, 28, 1. Presented Jan. 11, 1893.

BaBr, corresponding to 174.080 parts AgBr. Third, percentage of Ag in AgBr.

Exp.	I.	II.	III.
1.....	137.746	137.783	57.460
2.....	137.736	137.760	57.455
3.....	.....	137.723	.....
4.....	137.732	.....	.....
5.....	137.735	137.739	57.447
6.....	137.748	137.748	57.445
7.....	137.747	.....	.....
8.....	137.740	137.747	57.448
9.....	137.755	137.748	57.442
10.....	137.738	137.752	57.451
11.....	137.747	137.772	57.455
12.....	.....	137.726	.....
14.....	137.750	137.745	57.443
15.....	137.756	137.754	57.445
16.....	137.731	.....	.....
17.....	137.748	.....	.....
18.....	.....	137.745	.....
19.....	137.759	137.758	57.445
Mean, omitting 1 and 2.....	137.745	137.747	57.448
		Stas found....	57.445

The last column, by its agreement with Stas' measurements, serves to confirm the other two, from which the atomic weight of barium is easily computed. From the ratio  $\text{Ag}_2\text{BaBr}_2$ , when  $\text{Ag}=107.93$  and  $\text{Br}=79.955$ ,  
 $\text{Ba}=137.426$ .

From the ratio  $2\text{AgBr}:\text{BaBr}_2$ ,  
 $\text{Ba}=137.431$ .

The value 137.43 then must replace the lower value commonly held hitherto. The new results appear to be thoroughly established and unimpeachable.

*Thallium*.—Lepierre<sup>1</sup> has redetermined the atomic weight of this metal by several distinct methods. First, by the electrolysis of thallous sulphate in presence of an excess of ammonium oxalate, weighing first the sulphate and then the metal obtained. The latter was dried and weighed in an atmosphere of hydrogen. The corrected weights and results are as follows:

Wt. $\text{Tl}_2\text{SO}_4$ .	Wt. $\text{Tl}_2$ .	At. Wt. $\text{Tl}$ . ( $\text{O}=15.96$ ).
1.8935	1.5327	203.52
2.7243	2.2055	203.67
2.8112	2.2759	203.69

<sup>1</sup> *Bull. Soc. Chim.*, (3) 9, 166, March 20, 1893.

Secondly, a weighed quantity of crystallized thallic oxide was converted by means of sulphurous acid into thalious sulphate, which was then subjected to electrolysis as in the preceding series. The results are subjoined.

Wt. $Tl_2O_3$ .	Wt. $Tl_2$ .	At. Wt. $Tl$ .
3.2216	2.8829	203.76
2.5417	2.2742	203.53

In the third series of experiments a definite quantity of thalious salt was fused in a polished silver crucible with ten times its weight of absolutely pure caustic potash. Thallic oxide was thus formed, which was washed with water and alcohol under various precautions, dried at  $100^\circ$ , and finally weighed in the original crucible.

		At. Wt. $Tl$ .
3.1012 $Tl_2SO_4$ gave.....	2.8056 $Tl_2O_3$	203.57
2.3478 " " .....	2.1239 "	203.44
2.7591 $TlNO_3$ " .....	2.3649 "	203.73

Finally, crystallized thallic oxide was reduced in a stream of hydrogen, and the water so formed was collected and weighed.

Wt. $Tl_2O_3$ .	Wt. $H_2O$ .	At. Wt. $Tl$ .
2.7873	0.3301	203.54
3.9871	0.4716	203.82
4.0213	0.4761	203.00

The mean of the eleven figures given for thallium is 203.57, but stated by the author as 203.62. If  $O=16$  this becomes  $Tl=204.08$ ; and with  $O=15.88$ ,  $Tl=202.55$ . It will be observed that the values found in the individual experiments vary among themselves through a range of over eight-tenths of a unit, and that, therefore, the final mean result is entitled to little consideration. M. Lepierre is evidently unfamiliar with the determinations of his predecessors; for, quite ignoring the admirable work of Crookes, he speaks of the currently accepted value for  $Tl$  as resting without proof upon the calculations of Meyer and Seubert. He also neglects to state whether his weighings were reduced to vacuum standards, and he gives no evidence bearing upon the absolute purity and definiteness of the several compounds weighed. The metallic thallium which served as a starting point for the investigations, seems to have been carefully purified.

*The Composition of water by Volume.*—The volume ratio be-

tween H and O in water, which controls the atomic weight of oxygen as deduced from its density, has been redetermined by Scott.<sup>1</sup> The report published is only in abstract, but the subjoined values for the ratio,  $H_2:O$ , are given.

2.0020  
2.0024  
2.0026  
2.0030  
2.0022  
2.0025  
2.0029  
2.0023  
2.0028  
2.0017  
2.0022  
2.0028

Mean, 2.00245,  $\pm 0.00007$ .

Combining this mean with the density ratio,  $O:H::15.882:1$ ,<sup>2</sup> gives for the atomic weight of oxygen the value 15.862.

Scott gives mean results of several other series of experiments, but only this one in detail. The hydrogen was obtained from palladium hydride, and the oxygen from silver oxide. With only an abstract available, the work done cannot be critically compared with Morley's.

*The Density of the Principal Gases.*—These data, as determined by Lord Rayleigh,<sup>3</sup> having important bearing upon atomic weights, fall properly within the scope of this report. Full details are given as to the apparatus used, and all corrections are applied; such, for instance, as for the difference in volume of the glass globes when filled or exhausted, for the value of gravity at the laboratory in latitude  $51^{\circ}47''$ , etc., etc. The final results are as follows, with air as unity.

H..... 0.06960  
N..... 0.97209  
O..... 1.10535

The weights in grams per liter are:

<sup>1</sup> *Proc. Roy. Soc.*, 53, 130. Read March 23, 1893.

<sup>2</sup> Rayleigh.

<sup>3</sup> *Proc. Roy. Soc.*, 53, 134. Received March 4, 1893.

H.....	0.09801
N.....	1.25718
O.....	1.42952
Air .....	1.29327

Two of these constants have also been remeasured by Leduc;<sup>1</sup> who gives the following weights for one liter each:

Air.....	1.29315
N .....	1.2570

*Miscellaneous Notes.*—Richards and Rogers, in a paper upon the occlusion of gases by metallic oxides,<sup>2</sup> show that when the oxides of copper, nickel, zinc, and magnesium are prepared by the ignition of the nitrates, they retain appreciable quantities of gaseous impurities, such as nitrogen and oxygen, especially the former. The oxides of cadmium, mercury, lead, and bismuth, similarly prepared, contained no gaseous occlusion, excepting a mere trace in the case of cadmium. This observation reveals a possible serious source of error in several determinations of atomic weight, particularly in the cases of zinc and magnesium. In consequence of this fact, the atomic weight of zinc is now under reinvestigation in the Harvard laboratory, the compounds selected for study being the chloride and bromide.

In the study of the rare earths, rough determinations of atomic weight are of great importance in the identification of material. Commonly they are made by the sulphate method, which is familiar to all chemists. Gibbs,<sup>3</sup> however, in a study of these substances, makes use of the oxalates. By ignition, the oxide is left and can be weighed, while the proportion of oxalic acid is easily determinable by titration with permanganate solution. In some cases the oxalates were ignited with weighed quantities of pure sodium tungstate, the increase in weight representing  $R_2O_3$ . From the ratio between  $R_2O_3$  and  $C_2O_3$ , the molecular weight of the oxide is easily calculated, and agrees well with determinations made by the sulphate process.

Hinrichs, in a series of communications published in the *Comptes Rendus*,<sup>4</sup> attempts to show that Stas' determinations

<sup>1</sup> *Compt. rend.*, 117, 1072.

<sup>2</sup> *Proc. Amer. Acad.*, 28, 200. Presented May 10, 1893.

<sup>3</sup> *Am. Chem. J.*, 15, 546, November, 1893.

<sup>4</sup> On the  $KClO_3$  work, in 115, 1074. On the lead determinations, in 116, 431.

of atomic weights are vitiated by systematic errors, depending upon the quantities of material weighed. According to him the larger the weight of the substance employed the larger the error; and he constructs curves to represent his views graphically. His mathematical procedure, however, his "method of limits," is not clear, and it savors somewhat of assuming Proutian values in advance, and then regarding variations from them as errors for which corrections should be applied. At all events he fails to point out, on the basis of experimental evidence, how the supposed errors were produced, and he does not show that they could have been of sufficient magnitude to account for the divergencies to be explained. If Stas' work is to be set aside, it can be by experimental researches only.

In a third<sup>1</sup> paper the same author gives his mathematical process in some detail, and still later he discusses Dumas' experiments relative to the atomic weight of oxygen,<sup>2</sup> seeking to show that it is exactly sixteen. Very recently he has also discussed the determinations of the same constant made by Keiser, Cooke and Richards, Morley, and Dittmar and Henderson, reaching the conclusion that the ratio  $H:O=1:16$  rigorously.<sup>3</sup> He objects especially to the use of averages as fallacious, but does not fully establish the legitimacy of his conclusions.

In another journal<sup>4</sup> Hinrichs criticizes Richards' researches upon the atomic weight of copper. After showing that several published determinations of the electrolytic ratio between silver and copper agree quite well with the ratio  $108 : 63.5$ , he takes up in particular Richards' analyses of copper sulphate, and points out that a part of the data correspond with the even values  $O=16$ ,  $S=32$ , and  $Cu=63.5$ . The other work of Richards he dismisses as erroneous, but neglects to show wherein the errors lie.

In still another paper<sup>5</sup> Hinrichs proposes to abandon gases like O and H as bases for atomic weight determinations, and to

<sup>1</sup> *Compt. rend.*, 116, 695.

<sup>2</sup> *Compt. rend.*, 116, 753.

<sup>3</sup> *Compt. rend.*, 117, 663.

<sup>4</sup> *Chem. News*, 68, 171, October, 6, 1893.

<sup>5</sup> *Compt. rend.*, 117, 1075.



adopt carbon (diamond)=12 as the fundamental standard, on the ground that it can be exactly weighed. Oxygen and calcium are combined with this as substandards, becoming sixteen and forty respectively.

Replies to Hinrichs' criticism of Stas have been published by Spring<sup>1</sup> and by Van der Plaats.<sup>2</sup> Both writers object to the processes of extrapolation of which Hinrichs makes use, and Van der Plaats shows by tabulation of data that the systematic errors alleged to exist in Stas' experiments are not there. Only fortuitous errors occur, and these are of insignificant magnitude. Furthermore, the ratios determined by Stas are so numerous, so varied, and so concordant in their final results that the presumption in their favor is overwhelming.

In the same paper, indeed, as its main object, Van der Plaats gives the results of a recalculation of Stas' twenty-one ratios by the method of least squares. He does not, however, give his equations nor explain the special form of the method which he used. The results are stated in two tables, one, (A), computed upon the supposition that each ratio is entitled to weight inversely proportional to the square of its mean error; the other, (B), regarding all as of equal weight. O=16 is the base of the system.

	A	B
Ag .....	107.9244 $\pm$ 0.0136.	107.9202.
Cl .....	35.4565 $\pm$ 0.0049.	35.4516.
Br .....	79.9548 $\pm$ 0.0101.	79.9497.
I .....	126.8494 $\pm$ 0.0166.	126.8445.
S.....	32.0590 $\pm$ 0.0085.	32.0576.
K .....	39.1403 $\pm$ 0.0059.	39.1414.
Na .....	23.0443 $\pm$ 0.0043.	23.0453.
Li.....	7.0235 $\pm$ 0.0051.	7.0273.
Pb .....	206.9308 $\pm$ 0.0404.	206.9089.
N .....	14.0519 $\pm$ 0.0078.	14.0421.
NH <sub>4</sub> .....	18.0740 $\pm$ 0.0034.	18.0760.

Hence H= .. 1.0055  $\pm$  0.0021. 1.0085.

Another contribution to the Hinrichsian literature is furnished by E. Vogel,<sup>3</sup> who criticizes Stas at considerable length. His

<sup>1</sup> *Chem. Ztg.*, 17, 242, February, 22, 1893.

<sup>2</sup> *Compt. rend.*, 116, 1362.

<sup>3</sup> *Bull. Acad. Bruxelles*. (3), 26, 469.

paper is preceded by adverse reports from W. Spring and L. Henry.

In conclusion I submit a table of atomic weights revised to January 1, 1894. Oxygen=16 is taken as the base of the system, but for provisional reasons only. Before long, with improved determinations, it may be practicable to return to the more philosophical  $H=1$ , when the entire system can be transformed once for all into something like permanent shape. A premature transformation of this kind, however, would only work confusion, without corresponding benefit.

Name.	Atomic Weight.	Name.	Atomic Weight.
Aluminum.....	27.	Neodymium.....	140.5
Antimony.....	120.	Nickel.....	58.7
Arsenic.....	75.	Nitrogen.....	14.03
Barium.....	137.43	Osmium.....	190.8
Bismuth.....	208.9	Oxygen.....	16.
Boron.....	11.	Palladium.....	106.6
Bromine.....	79.95	Phosphorus.....	31.
Cadmium.....	112.	Platinum.....	195.
Caesium.....	132.9	Potassium.....	39.11
Calcium.....	40.	Praseodymium.....	143.5
Carbon.....	12.	Rhodium.....	103.
Cerium.....	140.2	Rubidium.....	85.5
Chlorine.....	35.45	Ruthenium.....	101.6
Chromium.....	52.1	Samarium.....	150.
Cobalt.....	59.	Scandium.....	44.
Columbium.....	94.	Selenium.....	79.
Copper.....	63.6	Silicon.....	28.4
Erbium.....	166.3	Silver.....	107.92
Fluorine.....	19.	Sodium.....	23.05
Gadolinium.....	156.1	Strontium.....	87.6
Gallium.....	69.	Sulphur.....	32.06
Germanium.....	72.3	Tantalum.....	182.6
Glucinum.....	9.	Tellurium.....	125.
Gold.....	197.3	Terbium.....	160.
Hydrogen.....	1.008	Thallium.....	204.18
Indium.....	113.7	Thorium.....	232.6
Iodine.....	126.85	Thulium.....	170.7
Iridium.....	193.1	Tin.....	119.
Iron.....	56.	Titanium.....	48.
Lanthanum.....	138.2	Tungsten.....	184.
Lead.....	206.95	Uranium.....	239.6
Lithium.....	7.02	Vanadium.....	51.4
Magnesium.....	24.3	Ytterbium.....	173.
Manganese.....	55.	Yttrium.....	89.1
Mercury.....	200.	Zinc.....	65.3
Molybdenum.....	96.	Zirconium.....	90.6

*Discussion.*—Dr. Wiley. By our organization we are able to present to American chemists the latest and most accurate numbers for atomic weights. It is a matter for congratulation that this has been accomplished by the American Chemical Society.

## UPON THE DETERMINATION OF NITRATES IN POTABLE WATER.

BY AUGUSTUS H. GILL.

Received February 29, 1894.

### PART II.

#### (b) THE REDUCTION TO AMMONIA.

AFTER a discussion of the various processes for the determination of nitrates by reduction to ammonia, Tiemann concludes with the following :<sup>1</sup> "On account of the unreliability and chances for error which this principle involves, we strongly advise against its use."<sup>2</sup> Tables are given, pp. 208 *et. seq.*, in which the results obtained by reduction with sodium amalgam, aluminum, and the zinc-copper couple, vary from plus ten to minus thirty-eight per cent. which sufficiently illustrate the unreliability.

The objections to any method for such reduction are in brief :

#### I. THE NUMEROUS CORRECTIONS TO BE APPLIED :

- I. For free ammonia.
  - II. For nitrates.
  - III. For materials used.
  - IV. For ammonia carried away by the hydrogen.
2. The liability of reducing the organic matter present in the water to ammonia.
  3. The time required and chances for error in manipulation. To the method proposed by Hazen and Clark,<sup>3</sup> they not distilling the reduced liquid before nesslerizing are added two more, *viz.* :
    4. The colors produced by the Nessler reagent are in many cases not the same *tone* as the standards, and are usually read higher than the amount of ammonia actually found by distilla-

<sup>1</sup> "Die chem. und bacteriologische Untersuchung des Wassers," Tiemann und Gaertner Braunschweig 1890, 212.

<sup>2</sup> "Entschieden davon abzurathen."

<sup>3</sup> *J. Anal. Appl. Chem.*, 5, 3.

tion;<sup>1</sup> see Nos. 2, 3, and 20 in the following table.

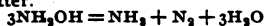
5. When the reduction is finished the liquid in the Nessler tube is not homogeneous, hence the removal of a portion without mixing—which at the same time occasions a troublesome turbidity—does not represent the amount of ammonia actually present.

All these objections might well be waived did the method yield reliable results; but as is shown in the accompanying tables, it is subject to even greater variations than the phenolsulphonic acid process.

RESULTS OF THE ESTIMATION OF NITRATES IN WELL WATERS BY THE ALUMINUM AND PHENOLSULPHONIC ACID METHODS.

		PARTS OF NITROGEN IN 100,000.				Differences	Nitrites.	Chlorine.
No.	P. S. A.	direct.	Aluminum crosswise.	distilled.	From P. S. A.	Per cent.		
1..	0.4000	0.4323	.....	.....	+0.0323	7	none	2.93
2*.	1.1500	1.0287	.....	0.9876	-0.1213	10	0.0001	2.78
		0.8306	0.7407	.....	-0.2194	23		
3*.	1.0000	0.8306	0.7407	.....	-0.1694	17	none	2.22
		0.8235	0.6995	0.7407	-0.1765	17		
4..	0.9000	0.8235	.....	.....	-0.0765	8	none	2.16
5..	0.0090	0.0041	.....	.....	-0.0049	50		
6..	0.0085	0.0041	.....	.....	-0.0044	50	none	0.34
7..	0.0500	0.0625	.....	.....	+0.0125	40		
8..	0.4500	0.3045	.....	.....	-0.1455	33	none	0.75
		0.3538	.....	.....	-0.0962	20		
9..	0.0060	0.0288	.....	.....	+0.0228	400	none	0.96
		0.0000	.....	.....	-0.0060	100		
10..	0.0140	0.0329	.....	.....	+0.0189	120	none	0.35
		0.0513	.....	.....	+0.0373	250		
11..	0.4200	0.3538	.....	.....	-0.0662	15	none	0.34
12..	0.0000	0.0000	.....	.....	.....	..		
13..	0.0400	0.0411	.....	.....	+0.0011	2	none	0.91
14..	0.3250	0.2472	.....	.....	-0.0778	21		
15..	0.7000	0.7242	0.6172	.....	+0.0242	3	0.0001	0.66
16..	0.7200	0.6748	.....	.....	-0.0452	5	0.0003	0.54
17..	0.2500	0.2634	.....	.....	+0.0134	5	0.0002	1.12
18..	0.3000	0.3127	0.2469	.....	+0.0127	4	0.0005	3.40
19..	1.0000	1.0287	.....	.....	+0.0287	3	0.0000	2.40
20*.	1.6000	1.3414	1.1522	.....	-0.2500	15	0.0002	2.57
		1.4418	.....	.....	.....	.....	.....	2.42
		1.3579	1.2345	1.3168	.....	.....	.....	.....

<sup>1</sup> The reason for the difference in tone of the reduced solutions is probably due to the presence of hydroxylamine, as the colors produced can be closely imitated by solutions of this compound. This is unaffected by the excess of alkali, and is with difficulty reduced to ammonia; upon distillation it breaks up into ammonia and nitrogen, thus giving rise to a loss of the latter.



By "crosswise" is meant the comparison of the tubes when looked through diametrically instead of axially as is customary; this was done, as the colors were not the same tone, to see if they could be matched more closely; the "distilled" column indicates the results as obtained by distilling a portion of the reduced liquid in addition to nesslerizing directly, it will be observed that these results are *lower* than those obtained by direct reading.

The method is supposed to be particularly valuable in the presence of relatively large amounts of chlorine; of eleven waters there given having a higher percentage than one part per hundred thousand, *five*, Nos. 1, 15, 17, 18, and 19, are estimated from 3-7 per cent. *higher* and *six*, Nos. 2, 3, 4, 14, 16, and 20, are estimated from 8-20 per cent. *lower* than the results of the phenolsulphonic acid process. Of the remaining waters three are estimated much too high and four as much too low.

Let us consider another table, this time of solutions made to contain definite quantities of nitrate; each letter represents a different and independent observer.

RESULTS OF THE DETERMINATION OF NITRATES IN STANDARD  
SOLUTIONS BY THE ALUMINUM AND PHENOL-  
SULPHONIC ACID METHODS.

PARTS OF NITROGEN IN 100,000.

No.	—Aluminum.—		Theory.	—Phenolsulphonic acid.—		
	A.	B.		C.	D.	E.
21 ..	0.0800	0.1080	0.0950	0.1020	0.1000	.....
22 ..	1.2800	1.3000	1.3500	.....	1.2000	1.3000 <sup>1</sup>
23 ..	0.0200	0.0140	0.0160	0.0200	0.0150	0.0180
24 ..	0.8000	0.9500	0.8500	0.8530	0.9500	0.9000
25 ..	2.0500	2.5000	2.2100	2.4500	2.5000	2.5000 <sup>2</sup>
26 ..	0.0400	0.0340	0.0380	0.0380	.....	0.0400
27 ..	0.0800	0.0660	0.0950	0.1000	0.1000	0.0930
28 ..	0.4200	0.3660	0.4250	0.4150	0.4500	0.4000
29 ..	0.4100	0.4040	0.4250	0.4500	0.4250	0.4000
30 ..	0.0300	0.0460	0.0350	0.0370	0.0270	0.0300
31 ..	0.0130	0.0120	0.0140	0.0215	0.0120	0.0150
32 ..	0.0130	0.0180	0.0140	0.0270	0.0150	0.0150
33 ..	0.0580	0.0640	0.0650	0.0620	0.0600	0.0550
34 ..	0.0610	0.0540	0.0650	0.0740	0.0520	0.0550
35 ..	0.0830	0.0880	0.0900	0.0900	0.0920	0.0700

<sup>1</sup> A later determination gave 1.3250.

<sup>2</sup> A later determination gave 2.1300.

No.	Aluminum.		Theory.	Phenolsulphonic.	
	Average.	Difference.		Average.	Difference.
21 .....	0.0940	—0.0010	0.0950	0.1010	+0.0060
22X .....	1.2900	—0.0600	1.3500	1.2500	—0.1000
23 .....	0.0170	+0.0010	0.0160	0.0176	+0.0016
24X .....	0.8750	+0.0250	0.8500	0.9010	+0.0510
25X .....	2.2750	+0.0650	2.2100	2.4833	+0.2733
26 .....	0.0370	—0.0010	0.0380	0.0390	+0.0010
27 .....	0.0730	—0.0220	0.0950	0.0976	+0.0026
28 .....	0.3930	—0.0320	0.4250	0.4216	—0.0034
29 .....	0.4070	—0.0180	0.4250	0.4250	0.0000
30 .....	0.0380	+0.0030	0.0350	0.0313	—0.0037
31 .....	0.0125	—0.0015	0.0140	0.0162	+0.0022
32 .....	0.0155	+0.0015	0.0140	0.0190	+0.0050
33 .....	0.0610	—0.0040	0.0650	0.0590	—0.0060
34 .....	0.0575	—0.0075	0.0650	0.0603	—0.0047
35 .....	0.0855	—0.0045	0.0900	0.0840	—0.0060
		—0.0915			—0.0238
		+0.0055			+0.0184

Numbers 22, 24, and 25 are very obviously incorrectly estimated by both methods; the aluminum process gave in two of these cases results too high; the phenolsulphonic acid process gave likewise in two cases results too high, probably from errors in reading caused by attempting to estimate too deep colors<sup>1</sup> (over 0.1300 parts nitrogen in 100,000).

Considering the other twelve determinations, the aluminum process gave results too low in nine, with a total of 0.0915 parts of nitrogen or *6.6 per cent. too low*, and too high in three with a total of 0.0055 parts of nitrogen or *0.4 per cent. too high*. The phenolsulphonic acid process gave too low results in five cases with a total of 0.0238 parts of nitrogen or *1.6 per cent. too low*, and too high in six cases with a total of 0.0184 parts of nitrogen or *1.3 per cent. too high*.

From this investigation it is evident that the aluminum method, in addition to being more troublesome to execute, yields results even in the presence of chlorine (two parts in 100,000) decidedly lower than the phenolsulphonic acid method: further than this, it was observed that duplicate determinations made by the former process did not present a satisfactory agreement.

<sup>1</sup> This the usual result.

This conclusion I am aware is in direct variance with the statement of Hazen and Clark,<sup>1</sup> who say, "This process (phenol-sulphonic acid) with proper precautions, gives results usually too low and often much too low."

In addition to the aluminum process, other methods of reduction have been studied: Fricke<sup>2</sup> states that Förster's—the reduction with metallic iron and caustic potash in presence of alcohol—Schmitt's—the reduction with iron and acetic acid—and Ulsch's,—the reduction by 'ferrum reductum' and sulphuric acid—all yield good results, provided 0.5 gram potassium nitrate be present, these are suitable for the valuation of saltpeters and are obviously not sufficiently refined for the purposes of water analysis. The other method of Ulsch<sup>3</sup> by reduction with iron and sulphuric acid and subsequent measurement of the "deficit of hydrogen" is open to the same objection. One milligram potassium nitrate is equivalent to 1.1 cc. of hydrogen, this corresponds to 1.38 parts nitrogen per 100,000.

Harrow's<sup>4</sup> method, the reduction to nitrate in presence of  $\alpha$  naphthylamine and sulphanilic acid is sensitive to 0.04 parts nitrogen per 100,000, or twenty times less delicate than the phenolsulphonic acid process. In my opinion advancement in the estimation of nitric acid for the purposes of water analysis is to be sought, not in any method of reduction to ammonia or nitrous acid, but rather in the formation of organic nitro bodies of high coloring power and constant composition, and with this the writer is already engaged.

In conclusion, I desire to express my indebtedness to Mrs. Richards, Miss Hyams, and Mr. Tuttle, of the Massachusetts Board of Health staff for assistance in making many of the above determinations.

MASS. INST. OF TECHNOLOGY,  
LABORATORY OF SANITARY CHEMISTRY,  
FEBRUARY, 1894.

<sup>1</sup> *J. Anal. Appl. Chem.*, 5, 3.

<sup>2</sup> *Ztschr. für angew. Chemie*, April, 1891. *Analyst* 16, 117.

<sup>3</sup> *Ztschr. anal. Chem.*, 20, 175. *Analyst* 16, 134.

<sup>4</sup> *J. Chem. Soc.*, 1891, *Trans.*, 320.

## DETECTION OF SALICYLIC ACID IN FOOD.<sup>1</sup>

By K. P. Mc ELROY.

SALICYLIC acid has been known for more than half a century, having been discovered in 1838 by Piria<sup>1</sup> in oxidizing the oil of meadow sweet (*Spiraea ulmaria*). But its commercial importance dates back only to 1874 when Kolbe<sup>2</sup> succeeded in making a synthesis of it from sodium phenolate and carbonic acid. In 1860, in conjunction with Lautemann, he devised another synthetic process<sup>3</sup>, but as this method involved the use of metallic sodium the product was expensive.

After securing the entire success of his second process in 1874, Kolbe turned his attention to finding uses for his product. In that and the succeeding year he published a number of papers on<sup>4</sup> its use as a food preservative, as did several of his pupils and assistants, etc.<sup>5</sup> Public attention became attracted to the acid and its use as a preservative spread with great rapidity. In 1877 the French Government<sup>6</sup> found itself obliged to take official action regarding the use in wine of salicylic acid.

Analytical chemists of course were not slow to recognize the new demand on their skill involved by the use of this substance as an addition to food, and methods for its detection were soon elaborated. The number of these methods has yearly increased and at present a fair sized bibliography of analytical literature relative to salicylic acid might be compiled.

The most useful properties of salicylic acid, analytically speaking are that it is volatile with steam, that it is extracted from acid liquids by ether, chloroform, carbon bisulphide or benzol, that it gives a bright purple color with ferric chloride, a green color with copper acetate, and a rose color when boiled with Millon's solution and that when converted into the methyl ester it gives rise to a characteristic odor of wintergreen. The iron test is the one which is universally used for the final recognition of this substance, the previous separation from the food being made either with one of the solvents above named or by distillation. It is extremely delicate, giving a good reaction with a tenth

<sup>1</sup> Read at the Baltimore Meeting, December 27, 1893.



milligram in twenty-five cc. of liquid. The copper test is not particularly delicate, nor is the methyl ester test, at least as far as I am concerned. This latter test has been brought forward particularly by Dr. Curtman, of St. Louis.<sup>7</sup> The test with Millon's solution is given by other substances extractable from foods by ether. The iron test is not given by any substance occurring in foods and extracted by ether to my knowledge. Carbolic acid gives the reaction nearest approaching it in color of the common substances, but this substance does not occur in food. Tannic acid, a little of which is sometimes taken up by ether from wines, gives a blackish or greenish color which has a tendency to hide the salicylic color.

In the laboratory of the Department of Agriculture the method which has been most commonly used involves the separation of the salicylic acid by distillation with water vapor. The use of distillation for this purpose, separating salicylic acid from food, I believe was first proposed in an unsigned article<sup>8</sup> appearing in the *Chemiker Zeitung*, in 1882, presumably from the pen of the editor, G. Krause. It was there stated that the method had been elaborated in the laboratory of that paper. Kolbe used distillation for the analytical separation of salicylic acid in 1880.<sup>9</sup> In using it in this laboratory on the samples of canned vegetables, the analyses of which are recorded in *Bulletin* 13, part 8, of the Division of Chemistry, United States Department of Agriculture, the contents of the can were pulped in a mortar, water added, together with a little phosphoric acid, the mixture strained through a bag, and the liquid subjected to distillation. The distillate was then collected in small portions and each portion separately tested with iron chloride. Mr. W. D. Bigelow who was associated with me in the analyses of these goods, and who made the greater portion of the tests, found the best strength of ferric chloride to be about five mgms. to the cc. The salicylic acid has a tendency to accumulate in the later portions of the distillate, and where the amount present is small, there will be hardly any test given by the first fractions. In illustration of this the following experiment may be adduced. Twenty-five milligrams of salicylic acid were dissolved in 250 cc. of water containing a little phosphoric acid and the mixture subjected to distillation, the distillate being collected in twenty-five cc. portions and the sali-

cylic acid estimated colorimetrically. The results may be tabulated as follows :

No.	cc.	Reaction.	Quantity found.
1	25	Distinct but pale.....	
2	25	Somewhat stronger .....	
3	25	Still stronger .....	0.3 mgm.
4	25	" .....	0.4 "
5	25	Bright .....	0.5 "
6	25	" .....	0.8 "
7	25	" .....	0.9 "
8	25	" .....	2.2 mgms.
9	15	" .....	3.0 "
Total.....			8.1 mgms.

I will quote in further illustration of this tendency the method for the determination of salicylic acid in wine described by M. Ince. In this method 210 cc. of wine are mixed with ten cc. of dilute sulphuric acid and the mixture subjected to distillation, the distillate being collected in fifty cc. portions. The first portion is thrown away and the acid estimated in the next two colorimetrically. The quantity found is multiplied by eight, it being assumed that one-eighth of the total salicylic acid will come over in those two fractions when using the amounts of liquid specified.

All the samples of canned vegetables were examined in this way using the fresh contents of the cans. Afterwards, for various reasons, I had the whole series gone over again and the extraction done in a different fashion. The residual contents of the cans had in the meantime been dried and ground to a powder capable of going through a hundred mesh sieve. Portions of this powder were made into a paste, or rather a very stiff dough, with dilute sulphuric acid, and the product placed in an ordinary ether extraction apparatus where it was extracted with ether for several hours. When the ether extract was evaporated to dryness and the residue taken up with water and distilled, the distillate gave the salicylic acid reaction with much greater brilliancy than had the original test, and many samples were found to contain the acid which had before given only doubtful tests or none at all in some cases. The cause of this difference was no doubt the imperfect extraction in the first method of separation, which practically gave only the salicylic acid present in the juice, while

the later method gave that existing in the solid portions as well. Many reactions were quite faint, so much so as to raise the question of the purpose of the addition of such minute quantities of salicylic acid. The smallness of these quantities was probably due, however, to a cause first pointed out by Kolbe<sup>9</sup> in 1880. Kolbe found that salicylic acid completely disappeared from wine and from water preserved in casks, while in similar samples preserved in glass this disappearance did not take place. Four months' standing, in some cases, were sufficient to cause this disappearance. As an experiment, he placed thoroughly washed cubes of different woods in glass flasks in contact with different solutions of salicylic acid and found that they caused a complete disappearance of the acid after various periods of time, while control samples in which no wood was placed retained their full content of salicylic acid. From the results of this work he drew the inference that woody tissue not only removed the salicylic acid from solution but caused its total destruction in some way, since he could not recover it from the cubes of woods used in the experiments just cited. The woody tissue of the canned vegetables may have caused an action similar to this.

We also use the ordinary "shaking out" method in the Department laboratory to some extent for such goods as beers and wines. The beer or wine is extracted with about half its volume of ether and the extract evaporated to dryness, and the residue taken up with warm water. The resultant solution is tested in the usual way with iron chloride. Between the two processes of separating the salicylic acid, distillation or shaking out with ether, I do not believe there is much choice, though the former is cheaper and more expeditious. The increased purity and sharpness of the reaction given by the distillate as compared with that given by the residue from the ether extract about counterbalance the fact that only a fraction of the salicylic acid appears in the distillate. Objections against the distillation process were raised in 1889 by certain Dutch chemists,<sup>10</sup> on the ground that in the process of fermentation certain "phenol-like bodies" were sometimes formed which interfered with the reaction. "Phenol-like bodies" would interfere not only with the distillation separation but with any other with which I am

acquainted, since phenol is taken up by immiscible solvents from acid solutions precisely as is salicylic acid.

This year three chemists,<sup>1</sup> writing for different German brewing papers, have claimed that in what is called "color" or "caramel" malt a substance exists which gives all the ordinary salicylic acid reactions. The substance is said to exist in many malt extracts rich in isomaltose. J. Brand isolated the substance from color malt and describes all its reactions as being analogous to those of salicylic acid with the single exception of that with Millon's reagent, with which the new substance gave no reaction. I procured a set of color and caramel malts from the World's Fair and tried to obtain a salicylic acid reaction from them, but could not do so. At my request Mr. Bigelow, who not long ago examined a large number of the beers exhibited at the World's Fair, tried a large number of them with Millon's reagent, using it side by side with the iron solution. He reported to me that the Millon's reagent gave salicylic acid in all the samples, irrespective of the reaction upon the ferric chloride. The latter gave salicylic acid in comparatively few. It is only just to say, however, that where ferric chloride indicated the presence of salicylic acid, the reaction given by Millon's reagent was much brighter than where this was not the case.

<sup>1</sup> Piria. Recherches sur la sâlicine et les produits qui en dârivent. *Ann. de chim. et de phys.*, 1838, 69, 281.

<sup>2</sup> Kolbe, H. Vorläufige Mittheilung. *J. prakt. Chem.*, 1873-4, 8, 41. Synthese der Paraoxybenzoesäure, *ibid*, 336. Ueber eine neue Darstellungsmethode und einige bemerkenswerthe Eigenschaften der Salicylsäure, *ibid*, 1874, 10, 89.

<sup>3</sup> Kolbe, H. and E. Lautemann. Ueber die Constitution und Basicität der Salicylsäure. *Liebig's Annalen*, 1860, 115, 201.

<sup>4</sup> Kolbe, H. Weitere Mittheilungen über die Wirkungen der Salicylsäure. *J. prakt. Chem.*, 1875, 11, 9; Darstellung chemisch reiner Paraoxybenzoesäure durch Umwandlung der Salicylsäure, *ibid*, 24; Weitere Mittheilung über die Wirkung der Salicylsäure, *ibid*, 213; Ueber die chemische Natur der Salicylsäure, *ibid*, 1875, 12, 151; Abweisung nicht begründeter Urtheile von Halbchemikern über die antiseptischen Eigenschaften der Salicylsäure, *ibid*, 161; Die chemische Natur der Salicylsäure, *ibid*, 151; Chemische Winke für praktische Verwendungen der Salicylsäure, *ibid*, 1876, 13, 106.

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<sup>5</sup> Fontheimer, Karl. Ueber die Wirkung der Salicylsäure als Arzneimittel. *J. prakt. Chem.*, 1875, 11, 211.

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Zürn. Die Salicylsäure in der Veterinärpraxis. *J. prakt. Chem.*, 1875, 11, 215.

<sup>6</sup> Fauvel, Bergeron and Bussy (reporter). Emploi de l'acide salicylique comme agent de conservation des vins. Report sur une demande d'avis adresse par la chambre de commerce de Paris. Recueil des travaux du comité consultatif d'hygiene 1877, 7, 346.

<sup>7</sup> Curtman, C. O. Nachweis der Salicylsäure durch Synthese des Gaultheriaöls. *Pharm. Rundschau*, 1885, 3, 155; *abs. Chem. Ztg.*, 1885, 9, 1504.

<sup>8</sup> Anonymous (G. Krause?). Nachweis von der Salicylsäure in Nahrungsmitteln. *Chemiker Ztg.*, 1882, 6, 619.

<sup>9</sup> Kolbe, H. Zerstörende Wirkung des Holzsubstanz auf Salicylsäure. *J. prakt. Chem.*, 1880, 21, 443 and 22, 112.

<sup>10</sup> Horn, G. A. [Detection of Salicylic Acid in Beer.] *Pharm. Weekblad* (1888?), Nos. 7 and 8; *Apoth. Ztg.*, No. 56; *Ztschr. Nahr. Hyg.*, 2, 150; *Chem. Centrbl.*, 1888, 1425.

<sup>11</sup> Erich, E. Ueber die Salicylsäurereaction der Caramelfarbmälze. *Bierbrauer*, 1893, 24, 465; *abs. Chem. Ztg. Rep.*, 1893, 17, 211.

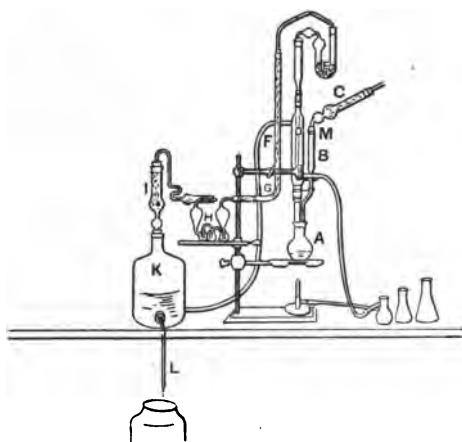
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## A CONVENIENT FORM OF APPARATUS FOR THE ESTIMATION OF CARBONIC ACID.

BY ROBERT H. FORBES.

**T**HE form of apparatus for the estimation of carbonic acid devised by the writer and shown herewith, has been fully tested in our laboratories and found to be accurate, cheap, compact, easily portable, and applicable both to the estimation of carbonic acid in carbonates and to that of carbon in iron by the



wet combustion with chromic and sulphuric acids. C is a tube, filled with solid potash, guarding the apparatus from the carbonic acid of the air. The small drop funnel B carries acid to the decomposing flask A. The small condenser D returns most of the water vapor, and the hydrochloric acid to the decomposing flask. The

small U tube E, containing a solution of silver sulphate in sulphuric acid, stops hydrogen sulphide and traces of hydrochloric acid. The drying tube F G, of one-half inch combustion tubing, and filled with calcium chloride, finally dries the carbonic acid gas before its absorption at H. The calcium chloride tube I guards the bulbs from moisture, and the aspirating bottle is discharged by the movable tube L.

When used for carbonates, a fifty cc. wide mouthed flask is best, but this must be replaced by a 250 cc. Erlenmeyer flask when making a wet combustion of carbon.

In practice it is found best, after the evolution flask is in position, to turn down the outlet tube L, and regulate the flow en-

tirely from the stop-cock B. Hydrochloric acid rarely gets beyond the condenser, and the downward pitch of the drying tube F G hastens the passage of the carbonic acid gas. The whole apparatus occupies less than two square feet of desk room.

CHEMICAL LABORATORY,  
UNIVERSITY OF ILLINOIS, AUGUST 25, 1893.

### THE SPECIFIC GRAVITIES OF SOME GEM STONES.<sup>1</sup>

BY A. LIVERSIDGE, M.A., F.R.S., PROFESSOR OF CHEMISTRY, UNIVERSITY OF SYDNEY.

THE following tables contain the specific gravities of some gem stones which were all in the cut and polished condition except in the cases specified. As the specimens were sufficiently free from flaws and mechanical impurities to be cut and polished for jewelry, the specific gravities can be taken as those of typically pure minerals and the results should be more satisfactory than those obtained from ordinary cabinet specimens, unless it can be shown that the specific gravity is altered by the pressure and other treatment they have received during the process of cutting and polishing.

The specific gravities were taken with special care on an Oertling's best chemical balance by direct weighing, *i. e.*, by suspending the specimen in a very small and light metal stirrup in distilled water. A specific gravity bottle was found, as is well known, to give less accurate results.

The temperature at the time of the determination is given in all cases and the results are corrected to 4° C. according to Rossetti's determinations of the density of water.

In the last column are given the extremes of specific gravity as given by F. W. Clarke in his Constants of Nature.

The numbers refer to those in my catalogue of specimens and added in case of future reference.

<sup>1</sup> Read before the World's Congress of Chemists, August 23, 1893.

No. of Spec.	Name.	Locality.	Temperature.	Weight.	Sp. Gr.	Corrected to 4° C.
63	BERYL Beryllium silico-aluminate.....		20° C.	0.1860	2.5399	2.5312
62	" (five small stones) pale green.....		"	0.5640	2.7865	2.7816
43	" " " " " "		21.5° C.	0.1225	2.7282	2.7228
39	" " " " " "		"	1.0108	2.6866	2.6773
F. W. Clarke gives a range from 2.690 to 2.725.....						
CHRYSOBERYL Beryllium aluminate.....		Ceylon.	19° C.	0.3615	3.4330	3.4277
Cymophane or cat's eye (three small stones).....		"	21° C.	1.8065	3.7147	3.7074
" " " " " "		"	"	2.1986	2.9299	2.9241
" " " " " "		"	19° C.	0.5193	3.6882	3.6825
" " " " " (four small stones).....		"	"	0.6445	3.7040	3.6982
F. W. Clarke gives a range from 3.597 to 3.860.....						
CHRYSOOLITE. Magnesium iron silicate.....			21.5° C.	0.2186	3.3839	3.3772
CORUNDUM. Alumina.....						
Adamantine spar.....		New South Wales.	21.5° C.	1.5550	3.9974	3.9895
Barklyite (four uncut stones).....		"	18.5° C.	0.5884	3.7382	3.7331
Ruby.....		Ceylon.	"	0.3257	4.0160	4.0081
" " " " " "		"	"	0.2644	4.0060	3.9981
" (six small stones).....		"	21.5° C.	0.3590	3.9977	3.9898
" star.....		"	19° C.	0.4230	3.9586	3.9525
" " " " " "		"	21° C.	0.1876	4.0960	4.0880
" " " " " "		"	20° C.	3.7932	3.9920	3.9850
F. W. Clarke gives a range from 3.511 to 3.994 for star ruby						
Sapphire, pale blue.....		New South Wales.	19° C.	0.3130	3.8882	3.8822
" royal blue.....		"	18° C.	0.1398	4.1117	4.1061
" " " " " "		"	19° C.	0.6486	3.9404	3.9343
" " " " " "		"	21.5° C.	0.2330	3.9827	3.9751
" " " " " "		"	"	0.4770	4.0219	4.0140
" (four) dark colored.....		Ceylon.	18.5° C.	0.5090	4.1124	4.1068
" " " " " "		"	20° C.	2.5580	3.9323	3.9254
" " " " " "		"	19° C.	0.8713	3.9730	3.9668
" " " " " "		"	20° C.	1.3668	3.9784	3.9714



No. of Spec.	Name.	Locality.	Temperature.	Weight.	Sp. Gr.	Corrected to 4° C.
7	Sapphire .....	Ceylon.	20° C.	1.2060	3.9476	3.9407
8	" .....	"	"	0.8220	4.0039	3.9959
1	yellow; large "Oriental topaz" .....	"	"	5.0802	4.0019	4.0019
16	" .....	"	19° C.	0.5956	3.9164	3.9103
2	star .....	"	"	1.1352	3.9943	3.9981
9	blue grey star .....	"	20° C.	4.4812	3.9914	3.9844
11	star .....	"	21° C.	2.8114	3.9959	3.9890
12	" .....	"	"	0.2973	4.0084	4.0085
29	" .....	"	19° C.	1.2374	3.9967	3.9905
F. W. Clarke gives a range from 3.962 to 4.022.						
23	Green sapphire or oriental emerald .....	New South Wales.	"	"	"	"
25	" (two small stones) .....	"	19° C.	0.2872	4.1146	4.1082
23	" .....	"	"	0.9674	4.0041	3.9979
25	" .....	Cudjoecong, N. S. W.	18.5° C.	0.5996	4.0733	4.0678
2	yellow .....	New South Wales.	20° C.	1.5972	3.9738	3.9668
3	" pale green .....	"	"	2.9772	4.0000	3.9930
DIAMOND .....						
61	Diamond, dark uncut octohedron .....	Bingera, N. S. W.	20° C.	0.2920	3.4762	3.4701
	" five dark colored, uncut .....	"	18.5° C.	1.3220	3.5633	3.5585
	" six light " .....	"	"	2.2790	3.5278	3.5230
F. W. Clarke gives a range from 3.334 to 3.350.						
16	FELDSPAR. Potassium aluminium silicate .....	"	"	"	"	"
17	Moonstone .....	"	"	"	"	"
18	" .....	"	"	"	"	"
F. W. Clarke gives a range from 2.5702 to 2.5950.						
	GARNETS .....	Ceylon.	21° C.	0.7370	2.5977	2.5826
44	Garnet, almandine. Iron aluminium silicate .....	"	"	0.3534	2.5833	2.5782
49a	" two specimens .....	"	"	0.2288	2.5823	2.5772
59	" three " .....	"	"	"	"	"
37	" two " .....	"	20° C.	"	"	"
41	" two " very dark .....	"	21.5° C.	0.2558	4.1399	4.1308
	" .....	"	"	"	4.0862	4.0792

No. of Spec.	Name.	Locality.	Temperature.	Weight.	Sp. Gr.	Corrected to 4° C.
60	Garnet.....	.....	20° C.	1.3768	4.0637	4.0666
64	" three specimens.....	.....	"	0.3280	4.1000	4.0998
65	" two " very dark.....	.....	"	0.2748	3.9458	3.9389
37a	" two " .....	.....	21.5° C.	0.5714	4.2515	4.2511
53	" cinnamon stone. Calcium aluminum silicate.....	.....	20° C.	0.4566	3.6448	3.6384
28	" " .....	.....	19° C.	0.4039	3.6400	3.6363
54	" " less full of air bubbles .....	.....	20° C.	0.5157	3.7342	3.7276
	F. W. Clarke gives a range for almandine of from 3.990 to 4.236. " " cinnamon stone " 3.235 to 3.609.	.....	.....	.....	.....	.....
50	LAPIS LAZULI, four pieces cut and polished for stud links.....	.....	21.5° C.	1.3560	2.7684	2.7699
46	PEARLS. Calcium carbonate.....	Ceylon.	21.5° C.	0.2841	2.7291	2.7237
47	Pearl, three specimens.....	Torres Straits.	"	1.1422	2.6837	2.6784
48	" " " very irregular .....	"	"	0.4510	2.6845	2.6792
	QUARTZ. Silica .....	.....	.....	.....	.....	.....
56	Rock crystal.....	.....	20° C.	0.2255	2.6877	2.6890
	F. W. Clarke gives a range from 2.61 to 2.697 at 0° C .....	.....	.....	.....	.....	.....
57	Amethyst .....	Oberstein	20° C.	0.4756	2.6481	2.6434
	" purchased at.....	.....	18° C.	5.2408	2.6965	2.6999
	F. W. Clarke gives a range from 2.699 to 2.744.....	.....	.....	.....	.....	.....
26	Rose Quartz, two specimens.....	Ceylon.	19° C.	1.1598	2.6674	2.6632
	F. W. Clarke gives a range from 2.651 to 2.698.....	.....	.....	.....	.....	.....
	Calngorm, purchased at .....	Oberstein.	18° C.	22.4670	2.6555	2.6519
	" " .....	"	"	15.6990	2.6553	2.6517
	" " " .....	"	"	13.3554	2.6997	2.6931
	" " brown " .....	"	"	3.9084	2.6997	2.6931
	F. W. Clarke gives a range from 2.651 to 2.698 (smoky).....	.....	.....	.....	.....	.....
8	Fibrous Quartz, "Cat's eye," .....	N. S. W., West. Dist.	18.5° C.	0.2636	2.6703	2.6667
34	Opal. Hydrous silica, two specimens.....	New South Wales.	19° C.	0.1150	2.0105	2.0074
35	" " " .....	.....	21.5° C.	0.1858	2.0690	2.0649
6	" " " flawed.....	"	19° C.	0.3616	2.0769	2.0746

No. of Spec.	Name.	Locality.	Temperature.	Weight.	Sp. Gr.	Corrected to 4° C.
8	SPINELS. Magnesium aluminate.....					
35	Spinel, dark blue.....	Ceylon.	18° C.	0.3306	3.6392	3.6343
36	" puce.....	"	21.5° C.	0.3468	3.5900	3.5899
	" dark puce.....	"	"	0.1616	3.5811	3.5761
	F. W. Clarke gives a range from 3.48 to 3.77.....					
1	TOPAZ. Aluminum silico-fluoride.....					
18	" ".....	New South Wales.	19° C.	1.5213	3.5602	3.5547
58	" ".....	"	18° C.	11.6010	3.5509	3.5461
32	" ".....	"	20° C.	0.6334	3.5110	3.5048
51	" two white.....	Ceylon.	21.5° C.	2.0280	3.5717	3.5647
31	" ".....	"	20° C.	0.4282	3.5330	3.5268
30	" yellow Brazilian.....	Brazil.	21.5° C.	0.3162	3.5728	3.5658
32	" pink " burnt.....	"	19° C.	1.0845	3.5466	3.5372
52	" ".....	"	20° C.	0.8920	3.5257	3.5195
13	" ".....	"	19° C.	0.4413	3.4676	3.4622
55	" ".....	"	20° C.	0.6585	3.5691	3.5628
	F. W. Clarke gives a range from 3.439 to 3.597.....					
12	TOURMALINE. Aluminum boro-silicate.....					
	" brown colored specimen.....	Ceylon.	19° C.	0.4835	3.0687	3.0640
	F. W. Clarke gives a range from 2.997 to 3.243 and from 3.035 to 3.068 for brown tourmalines.....					
5	TURQUOISE. Hydrous aluminum phosphate.....	Sinai.	19° C.	0.3440	2.7388	2.7345
	F. W. Clarke gives a range from 2.426 to 2.651.....					
4	ZIRCONS. Zirconium silicate.....					
9	Zircon, red.....	New South Wales.	19° C.	0.4026	4.4753	4.4714
10	" ".....	"	18° C.	0.3118	4.7822	4.7757
14	" cut and polished.....	"	18.5° C.	1.8145	4.7191	4.7127
	" pale green.....	"	19° C.	0.4160	4.5921	4.4951
	F. W. Clarke gives a range from 4.047 to 4.709 at 21° C.....	Ceylon.				

## NOTES ON THE GRANDEAU METHOD FOR THE DETERMINATION OF HUMUS IN SOILS.

BY HARRY SNYDER.

Received January 18, 1894.

THE Grandeau method for the determination of humus in soils, without some modifications, is open to serious objections: (1) It is difficult to obtain a complete extraction of the humus materials with ammonia, as ordinarily carried on, especially when the soil is very fine and of a clayey nature. (2) The filtration is frequently so slow that a week is sometimes required before the filtrate becomes clear. (3) During all of this time the laboratory is so filled with fumes of ammonia as to seriously interfere with other lines of work.

To say the least, the present method is slow, cumbersome, and gives unsatisfactory results with many kinds of soils. The author has had in use during the past year, a few simple modifications, that have given good results.

After treatment with the dilute acid, the soil is transferred to either a glass-stoppered bottle, or a glass-stoppered Erlenmeyer flask of 100 cc. capacity, using fifty or sixty cc. of the dilute ammonia solution for that purpose. The contents of the bottle or flask are then well shaken at frequent intervals, and then allowed to settle. After settling, the dark colored solution is decanted into a filter, a fresh fifty cc. portion of the dilute ammonia solution is then added to the flask, and the same treatment repeated. It usually requires three or four such treatments before the filtrate becomes clear; the contents of the flask are then brought on to the filter, and require but little farther washing in the usual way before this part of the operation is completed. While the second, third, and fourth treatment with the ammonia is being carried on, the first portion of the filtrate can be evaporated on the water bath, and thus save time when that part of the operation is reached. The most progress can be made by making as large a number of determinations at one time as a person can conveniently take care of, so as not to unnecessarily hurry the operations, nor lose too much time in

making the humus determinations of the soil. A separate room for such work is a great convenience.

The results obtained by this method of treatment are much higher than those obtained when working in the usual way. This is to be expected, inasmuch as more complete extraction of the humus materials are obtained by using the glass-stoppered flasks. Duplicate results with the ordinary Grandeau method are far from being concordant, while with the glass-stoppered flasks reasonably concordant results are secured.

The Grandeau method for the determination of humus, when properly carried out, is capable of giving results that are of practical agricultural value. The examination of a few typical cases out of over a hundred samples of soil examined in the laboratory of the Minnesota Experiment Station, during the past two years, will show that the results obtained by the modified Grandeau method are well worth all of the time and labor that has been spent. Before examining the results, two points are to be noted:

*First.* There are many other organic compounds of equal agricultural value that are not included in the ammonia extract. Take for example any of the soils that show from ten to fifteen per cent. of volatile matter. The combined water, carbon dioxide, and humus, as well as volatile mineral matters account for sixty to seventy-five per cent., only, of the volatile material, leaving twenty-five per cent. of the volatile organic materials not accounted for. These organic materials, may, in time, become soluble in the ammonia solution, and finally be classed as humus materials. The Grandeau method gives us no idea of the extent to which these organic substances may be present in the soil.

*Second.* Along with the humus soluble materials are variable amounts of phosphoric acid. A careful study of the total phosphates, humus and phosphates soluble with the humus fails to indicate any chemical combination between the humus and the ammonia soluble phosphates. At this point another serious difficulty presents itself: Some soils which are rich in both phosphoric acid and lime, will give up some of their phosphoric acid to the dilute hydrochloric acid solution

that is first used to remove the lime. This appears to be quite prominent with some of the native soils that are particularly rich in total phosphates, humus, and lime. The analyses of many of these soils showed that the phosphates soluble in the dilute ammonia, and supposed to be in combination with the humus as available phosphoric acid, was less, in many soils, even when the humus was found to be high, than in other soils that were known to be far less fertile. A repetition of the work showed that the dilute hydrochloric acid used in removing the high percentages of lime, also removed a large portion of the phosphates that would have been soluble in the ammonia. Is not this phosphoric acid equally as valuable, agriculturally, as that soluble in the dilute ammonia? Qualitative tests can easily be made of the hydrochloric acid washings, to determine the presence or absence of phosphates.

In the native soils there is quite a close relation between the humus, as determined by the modified method, and the total nitrogen. The table given, shows the amounts of humus and nitrogen, as well as the ratio between the two, in a number of native soils, and soils that have been cultivated for various periods without the use of fertilizers. The volatile matter given includes both the total organic matter and the combined water, the carbon dioxide, hygroscopic moisture, etc., having been separately determined and subtracted from the total volatile matter.

RATIO OF NITROGEN TO HUMUS.

Description of soil.	No. of soil.	Total	Total		Ratio.
		volatile	Humus	nitrogen	
		per cent.	per cent.	per cent.	
Virgin soil .....	203	15.55	5.34	0.38	13.97
10 years cultivation .....	298	5.58	3.02	0.25	12.10
Virgin soil .....	202	8.10	5.16	0.41	12.60
10 years cultivation .....	236	5.48	2.87	0.21	13.60
Virgin soil .....	272	14.29	5.16	0.39	13.23
8 years cultivation .....	309	9.67	3.16	0.25	12.60
6 " " .....	224	10.90	5.12	0.38	13.20
Native prairie .....	224	12.05	4.04	0.37	10.91
10 years cultivation .....	312	8.15	2.60	0.22	11.80
6 " " .....	249	11.50	4.92	0.41	12.00
10 " " .....	208	7.13	2.68	0.24	11.18
8 " " .....	210	4.04	3.02	0.24	12.60

Description of soil.	No. of soil.	Total volatile per cent.	Humus per cent.	Total nitrogen per cent.	Ratio.
10 years cultivation.....	257	8.68	2.48	0.19	13.10
15 " " .....	234	6.47	2.48	0.20	12.40
3 " " .....	220	12.40	4.17	0.37	11.28
3 " " .....	218	6.56	3.73	0.30	12.43
20 " " .....	261	8.73	2.84	0.26	11.31
30 " " .....	279	8.31	1.80	0.16	11.25
40 " " .....	242	7.04	2.41	0.21	11.50
6 " " .....	222	10.33	3.42	0.28	13.00
18 " " .....	269	9.44	3.91	0.34	11.50
25 " " .....	290	3.54	2.27	0.17	13.35
6 " " .....	273	8.13	4.18	0.37	11.33
18 " " .....	249	7.94	2.04	0.17	12.00

There is, on the average, about twelve parts of humus in the soil, as determined by the method given, to every one part of nitrogen. In the long cultivated soils which have received no fertilizers, the nitrogen and the humus have decreased in about the same ratio. The losses and relationships are not in strict accordance to a mathematical ratio, but it is sufficient to show that there is a relationship between the humus and the nitrogen in a virgin soil, and in soils which have been cultivated without the use of fertilizers.

UNIVERSITY OF MINNESOTA,  
LABORATORY OF THE  
COLLEGE OF AGRICULTURE.

### NOTES.

*The Opening of the Kent Chemical Laboratory of the University of Chicago.*—In response to invitations sent out by the authorities of the University of Chicago to the chemists throughout the country to be present at the formal opening exercises of the Kent Chemical Laboratory, January 1 and 2, 1894, about fifty chemists assembled in the auditorium of the laboratory, at two o'clock P. M., January 1. It was proposed that the first meeting should be a conference of teachers of chemistry. President Harper delivered a brief address of welcome and closed by saying that Prof. Remsen had consented to act as chairman of the conference—Prof. Remsen then took the chair and after a few introductory remarks introduced Prof. Paul C. Freer, of the

University of Michigan, who had been invited to open the discussion by reading a paper on, "The Teaching of Chemistry in Secondary Schools and Colleges." After Prof. Freer's paper which was very suggestive, a general and spirited discussion ensued which was alike enjoyable and helpful to all present.

At six o'clock dinner was served at the hotel Windermere to the visiting chemists who were the guests of the University. The dinner was elegant in every particular. No "after dinner speeches" were made but during the progress of the courses president Harper announced that it had been proposed that the chemists present, organize a chemical society of some sort and as he knew very little about it he would call on Prof. Nef to state the nature of the proposed plan—Prof. Nef said that the idea was to organize a society of teachers of chemistry to meet at least once a year to discuss methods of teaching chemistry. He invited discussion and after remarks by a few chemists, a motion was made and carried, referring the whole subject to a committee, to be appointed by the chairman, to report to a meeting to be held the next morning at nine o'clock, in the auditorium of the Kent Laboratory. President Harper asked Prof. Remsen to appoint the committee, and he named: Profs. A. B. Prescott, J. U. Nef, P. S. Baker, W. W. Daniells, and A. V. Young.

Immediately after the dinner the chemists returned to the auditorium of the laboratory where at eight o'clock the dedicatory exercises began. President Harper with Mr. Sidney A. Kent headed the procession, followed by Prof. Remsen, Rev. Dr. Northrup, Prof. Nef, the visiting chemists and the faculty of the University. The visiting chemists occupied front seats in the audience while the speakers, Mr. Kent, and the faculty sat on the platform. The dedicatory prayer was delivered by Dr. Northrup, of the University of Chicago. President Harper then delivered a short address in which he read the letter of donation from Mr. Kent. It was as follows:

"Mr. William R. Harper, president of the University of Chicago—My Dear Sir: I hereby give this building, fully furnished and completely equipped, to the University of Chicago as a chemical laboratory for the use of this and future generations. Trusting that the standard of educa-



tion will be such as to command the respect not only of this country but of the civilized world.

Very Truly Yours,

"Chicago, Jan. 1, 1894."

S. A. KENT.

Prof. Ira Remsen, of Johns Hopkins University, who had planned the laboratory was then introduced. He made a very graceful address and at the close he thanked Mr. Kent in behalf of the chemists of the country for the substantial aid he had given the science in building so magnificent and complete a workshop.

Prof. J. U. Nef, under whose immediate supervision the laboratory had been built, and who planned most of the detail of the interior fittings was then introduced. He delivered an interesting address entitled, "Important Factors in the Development of a Research Laboratory."

At the conclusion of Prof. Nef's address, president Harper called on Prof. A. B. Prescott, of the University of Michigan, as the oldest teacher of chemistry present to make some remarks. Prof. Prescott delivered a brief impromptu address in his usual happy and pointed style. At the conclusion of the addresses a reception was held in the Halls of the laboratory.

The laboratory and equipment has cost Mr. Kent \$235,000.00, and it is very handsome, convenient and complete. It is to be hoped that the plan with detailed description will be published before long.

Mr. Kent is the brother of the founder of the Kent Chemical Laboratory, of Yale University. In the vestibule of the main entrance on the east wall in a handsome medallion bas-relief of Mr. Kent and below it is the dedicatory inscription which reads thus:

"This building is dedicated to a fundamental science in the hope that it will be a foundation stone laid broad and deep for the temple of knowledge in which as we live, we have life.—Sidney A. Kent."

On the morning of January 2, at nine o'clock, the visiting chemists assembled to hear the report of the committee appointed the night before at the dinner. The report provided for a conference of chemists to be held annually at such time and place as may be decided each year by the conference. No organization was made other than the formation of a standing

committee of three (3) members who are to make the necessary arrangements for the meeting, the chairman of the committee is to act as secretary of the conference. The committee for 1894 consists of Profs. J. U. Nef, P. S. Baker, and P. C. Freer. The object of the conference is to discuss methods of teaching and no papers on research are to be read. The meetings are to be arranged so as not to conflict with the meetings of the American Chemical Society and it was the sense of the meeting that whenever possible the conference should be held in conjunction with the meeting of the American Chemical Society.

The Winter Convocation of the University was held in Central Music Hall, January 2, at eight o'clock P. M. The convocation address being delivered by Prof. Ira Remsen who took as his subject, "The Chemical Laboratory." He spoke of the origin and development of the modern chemical laboratory and of the character of the work which had been done in the great laboratories of the world; of the work which had been accomplished in this country and of the prospects for the future. His address was highly entertaining and was enjoyed by a large audience composed of the faculties, official guests, students, and friends of the University. After the exercises a reception was held by the president in honor of Prof. Remsen in the foyer of the Music Hall.

The committee of arrangements who had charge of all of the exercises consisted of Profs. J. U. Nef, R. D. Salisbury, C. A. Strong, W. S. Stratton, and J. Loeb.

They are to be congratulated on the success of their management.

W. L. DUDLEY.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### AN ATTEMPT TO FIND THE AMOUNT OF PHOSPHORUS IN THREE SAMPLES OF STEEL.<sup>1</sup>

BY CHAS. B. DUDLEY, AND F. N. PEASE, Chemist and Assistant Chemist,  
Pennsylvania Railroad, Altoona, Pa.

SOMETHING over a year and a half ago, in connection with the preparation of a method for determining phosphorus in steel, to be used as a part of the specifications on which steel is bought, for the use of the Pennsylvania Railroad Company, we deemed it essential to know pretty accurately, the amount of phosphorus in each of three different samples of steel. The use made of the results finally obtained from these steels, is given in our paper, "On Some Points in the Determination of Phosphorus in Steel by the Volumetric Method," and what follows here, is an account of the various efforts made to get the desired information. It will be observed before we have finished, that what at first seemed a very simple thing, proved in the end to be a very difficult affair, and that after all the work done on the subject, the final result is still not entirely free from doubt.

The three samples of steel were as follows: No. 1 was boiler plate made by the open hearth process, and containing presumably about 0.15 per cent. of carbon, and less than 0.05 per cent. of phosphorus. No. 2 was a piece of a locomotive driving tire, made by the open hearth process, and containing presumably from 0.50 per cent. to 0.60 per cent. of carbon and

<sup>1</sup> Read at the Baltimore meeting, December 28, 1893.

from 0.05 per cent. to 0.07 per cent. of phosphorus. No. 3 was a crucible steel billet, containing presumably from 1.00 per cent. to 1.20 per cent. of carbon and less than 0.04 per cent. of phosphorus. Quite a quantity of drillings from each of these samples was prepared, care being taken to eliminate the influence of segregation as much as possible by (1) putting the drill holes entirely through the sample, and at right angles to the line of final solidification of the metal, (2) by having the drillings as fine as they could conveniently be made, and (3) by thoroughly mixing them.

The drillings having been obtained, our first thought was that we would find out the amount of phosphorus in these steels, by analyzing them ourselves, and by asking some other chemists of recognized ability, to do the same. Accordingly a quantity of the drillings was sent to four different chemists: Mr. A. A. Blair, 406 Locust street, Phila., Dr. T. M. Drown, Mass. Inst. Tech., Boston, Prof. J. W. Langley, Case School of Applied Science, Cleveland, O., and Mr. A. S. McCreath, Harrisburg, Pa. Blair used the acetate method; Drown the molybdate-magnesia method; McCreath the acetate method; Langley both these methods, and we ourselves used the molybdate-magnesia method on all the samples, and the acetate method on the No. 2 sample. We are without information as to the exact details of the methods used by the other chemists. In our own case we used the molybdate-magnesia method, exactly as described in Fresenius' Quantitative Analysis, second American edition, John Wiley and Sons, p. 763, except that we used five grams dissolved in concentrated nitric acid, instead of aqua regia, and heated to 200° C. in an air bath, as suggested by Blair in The Chemical Analysis of Iron, second edition, p. 90, in order to destroy carbonaceous matter. In using the acetate method we proceeded exactly as described in The Chemical Analysis of Iron, by A. A. Blair, second edition, p. 81, and following. We give below the results that have been obtained on these three samples of steel, in accordance with the above, as follows:

	No. 1. Per cent.	Steel. No. 2. Per cent.	No. 3. Per cent.
Blair .....	0.035	0.041	0.029
Another operator.....	0.035	0.047	0.027
Third operator.....	0.035	0.047	0.028
Drown, average of duplicates .....	0.037	0.050	0.030
McCreath .....	{ 1.... 0.035	0.045	0.027
	{ 2.... 0.035	0.046	0.028
Langley..	{ Acetate method ....	0.053	0.019
	{ " " ....	....	0.020
	{ Another operator....	0.050	0.019
	{ " " ....	0.056	0.020
Langley, molybdate magnesia .....	0.040	0.053	0.022
Dudley	{ Molybdate magnesia { 1.... 0.041	0.056	0.033
	{ 2.... 0.042	0.056	0.032
	{ 3.... 0.041	0.056	0.033
and Pease	{ 1.... ....	0.047	....
	{ Acetate method ....	0.046	....
	{ 2.... ....	0.046	....
	{ 3.... ....	0.046	....

It will be observed that these results are hardly as satisfactory as could be desired, and that if we must know as we very greatly desired to do, within a couple of thousandths of a per cent. the amount of phosphorus actually in these steels, we were thus far without this information. The extreme variation on the No. 1 steel, is from 0.035 per cent. to 0.042 per cent. a difference of 0.007 per cent. the average of the thirteen determinations being 0.0386 per cent. On the No. 2 steel, the range is from 0.045 per cent. to 0.056 per cent. a difference of 0.011 per cent., the average of the sixteen determinations being 0.0512 per cent. On the No. 3 steel, the range is from 0.019 per cent. to 0.033 per cent., a difference of 0.014 per cent., the average of the fourteen determinations being 0.0262 per cent.

In view of these results some further study was put upon the matter. It will be observed that in our own hands, the molybdate-magnesia method, and the acetate method, do not give the same results, nor do they give the same results in the hands of Langley, and we accordingly were somewhat in doubt, as to which method gave the most reliable results. In order to locate if possible the difficulty, we examined all the residues obtained, in the course of the acetate method, and to our astonishment we found phosphorus in three different places, which we will now describe.

I. It will be remembered that after the phosphorus is separated from the bulk of the iron, by means of the basic acetate precipitate, there is quite a volume of filtrate, containing iron in the protoxide form. This filtrate was allowed to stand in the beaker for a couple of days covered, and at the end of this time, the bottom of the beaker contained quite a precipitate of apparently hydrated sesquioxide of iron, which separated on standing. This precipitate was filtered off, and dissolved in dilute nitric acid and tested with molybdate solution. In no case did we fail to get a little yellow precipitate, apparently indicating that the amount of sesquioxide of iron obtained in the solution, before the basic acetate separation is made, is not quite sufficient to, or does not succeed in carrying down all the phosphorus. The directions require that a few drops of bromine water should be added, to oxidize enough iron to combine with the phosphorus, which was carefully done in every case, but so far as these experiments go, they seem to indicate that some of the phosphorus is still left behind.

II. It will be remembered that the basic acetate precipitate, is dissolved on the filter in hydrochloric acid. In our working of the acetate method, we found in a number of cases, a slight amount of material left undissolved on the filter. On collecting the filters from a number of determinations, burning off the filters, dissolving with nitric acid, and testing with molybdate, a clear reaction for phosphorus was obtained. It should be stated that the stain left on the filter paper, after dissolving in hydrochloric acid, is not in our experience universal. Under certain conditions the basic acetate precipitate apparently goes up with greater difficulty, than with others. It is also claimed that when titanium is present in iron or steel the basic acetate precipitate usually leaves a stain on the filter.

III. The filtrate from the ammonium magnesium phosphate, which it will be remembered contains some iron, and some citric acid, was treated with dilute nitric acid and evaporated to dryness on the steam table. The residue was taken up with dilute nitric acid and treated with molybdate, and here a voluminous yellow precipitate was obtained.

These experiments seemed to indicate that, in our hands at

least, the acetate method did not give quite all the phosphorus, and helped to explain the discrepancy between the molybdate-magnesia method and the acetate method. The bulk of the yellow precipitate obtained in the three places above described, especially from the citric acid filtrate, was so considerable that it seemed almost possible to get a sufficient amount of phosphorus from it to weigh, and we accordingly made three more determinations on ten (10) grams each of the No. 2 steel, by the regular acetate method, obtaining as the average of the three 0.045 per cent. The residues from the three places above described from these thirty (30) grams of steel were all collected together and the phosphorus separated from these residues by means of molybdic acid. The yellow precipitate obtained was then treated with magnesia mixture in the regular way. The results gave a percentage of 0.0053 per cent. phosphorus, and this added to the amount obtained by the direct acetate method gave the phosphorus in the No. 2 sample 0.0503 per cent. This figure it will be observed is 0.006 per cent. less than the average which we obtained on the same sample by the regular molybdate-magnesia method.

It has generally been conceded, we think, that the molybdate-magnesia method for determining phosphorus, following Fresenius, is liable to give rather high results, especially if arsenic is present and is not separated, which we did not do. We did separate the possible traces of silica from the magnesium pyrophosphate as Fresenius recommends. We were therefore still in doubt as to the amount of phosphorus in these steels, and did not feel satisfied to use any of the results obtained.

The question therefore arose with renewed force, how shall we find out how much phosphorus these three steels contain? After considerable study and discussion, the following method was decided on, namely: Start with ten grams, and proceed exactly as described in *The Chemical Analysis of Iron and Steel*, above mentioned, up to the point of adding the bromine. Then instead of adding a few drops, add enough bromine water to convert half a gram of the iron into the sesquioxide. Then make the basic acetate separation as described, except on account of the large amount of iron, a little ammonium acetate is

added. Dissolve the basic acetate precipitate in moderately strong hydrochloric acid, and evaporate the liquid to dryness, to render any silica present insoluble. Take up with forty cc. of strong nitric acid, and evaporate to dryness a second time, to remove the hydrochloric. Then take up with seventy-five cc. of dilute nitric acid, 1.13 sp. gr., filter, and precipitate with seventy-five cc. of molybdate mixture, with the proper precautions of the molybdate-magnesia method as to temperature and time. Collect the yellow precipitate on a filter, and after thorough washing dissolve in  $2\frac{1}{2}$  cc. of strong ammonia diluted with water, and wash thoroughly with water until the total volume of solution amounts to about 100 cc. Pass hydrogen sulphide until this solution becomes dark red in color. The hydrogen sulphide readily converts the molybdic acid into molybdenum sulphide, in ammoniacal solution, and if the gas has been passed long enough, a complete separation of the molybdic acid results when the solution is treated with hydrochloric acid in slight excess. Filter off from the molybdenum sulphide, wash thoroughly with water containing a little hydrochloric acid, and evaporate nearly to dryness, in order to have controllable bulk of solution. Then take up with a little water, to which two or three cc. of dilute hydrochloric acid has been added, and filter if necessary to remove separated sulphur and a trace of molybdenum sulphide which may separate during the evaporation. Concentrate the filtrate to about fifteen cc., and add five cc. of magnesia mixture, and a little ammonia. The total volume of the solution should not now exceed twenty-five or thirty cc. The ammonium magnesium phosphate from this point is treated in the regular way.

The three samples of steel above referred to treated in this way, gave the following figures:

	No. 1.	No. 2.	No. 3.
	Per cent.	Per cent.	Per cent.
Phosphorus .....	1 ..... 0.040	0.053	0.032
	2 ..... 0.040	0.054	0.033

Unfortunately the separated oxide of iron from the filtrates in the basic acetate separation, in the cases of these determinations were not examined, but subsequent examinations of this material on other samples has shown that half a gram of iron



carries down all the phosphorus, or possibly all but the merest trace. Also in the case above mentioned, nothing was left on the filter when dissolving the basic acetate in hydrochloric acid. An examination of the filtrate from the magnesium phosphate precipitate in no case failed to show a slight yellow precipitate, and these results have been confirmed by quite a number of subsequent examinations. The amount of this, however, is very slight, the bulk of the yellow precipitate obtained being very much less than is shown in the citric acid filtrate when the acetate method is used. It seems probable therefore, that notwithstanding all the precautions involved in the method described above, the results given are still a trifle low. These figures were, however, taken as representing the phosphorus content of these three samples of steel.

The method finally used on these steels, and whose results we regard as the most reliable, will be at once recognized as a modification of the combination method, first proposed by Riley, and subsequently described in detail by J. Lawrence Smith in the *American Journal of Science*, 123, 316. This combination method seems to have several advantages and perhaps to unite, in a sense at least, the best features of the acetate and the molybdate-magnesia methods. The acetate method is used to concentrate the phosphorus from a large amount of material, into a very small amount of iron. The molybdate method is used to separate the phosphorus from the iron. The conversion of the molybdic acid into sulphide in ammoniacal solution is due to a suggestion of Hundeshagen. It will be observed that by the method as we actually used it there are two opportunities to get rid of arsenic, *viz.*, before the basic acetate precipitation is made, and also along with the molybdenum sulphide. Subsequent experiments seemed to indicate that the first of these two separations can be omitted with safety. The method is long and laborious, but seems to offer, all things considered, perhaps the most accurate means now known of determining small amounts of phosphorus in steel. It may be well to add that on coming subsequently to determine phosphorus in these three steels by the volumetric method, a difficulty was found with the No. 2 steel. This will appear by a comparison of the

results obtained on the three steels by the two methods, as follows:

	No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.
Combination method.....	0.040	0.053	0.032
Volumetric method.....	0.040	0.059	0.032

In view of this discrepancy an arsenic determination was made on the No. 2 steel, following exactly the method described in *The Chemical Analysis of Iron*, p. 188, except that we started with fifty grams. The result obtained was

	No. 2. Per cent.
Arsenic .....	0.009

This result seems to indicate that arsenic is the cause of the discrepancy in the No. 2 steel, and apparently confirms again the view that arsenic interferes with the determination of phosphorus by means of molybdic acid.

It is perhaps not essential but may not be amiss to say that where the amount of phosphorus is large a difficulty may arise with the combination method, if ten grams are used to start with, due to the large bulk of molybdenum sulphide obtained. Very large amounts of molybdenum sulphide are difficult to wash clean. Of course the difficulty is easily overcome by starting with less than ten grams.

### ON SOME POINTS IN THE DETERMINATION OF PHOSPHORUS IN STEEL BY THE VOLUMETRIC METHOD.<sup>1</sup>

By CHAS. B. DUDLEY AND F. N. PEASE, Chemist and Assistant Chemist,  
Pennsylvania Railroad, Altoona, Pa.

ONE of the most common methods of separating phosphorus from iron, either in ores, pig iron, wrought iron or steel, is by means of molybdic acid, the separation giving rise to the well-known yellow precipitate of ammonium phosphomolybdate. The subsequent treatment of this yellow precipitate is very varied. Some chemists prefer to dissolve the precipitate in ammonia, and then determine the phosphoric acid by means of magnesia mixture. Others prefer to weigh the yellow precipitate just as obtained, and some even to measure the volume of

<sup>1</sup> Read at the Baltimore meeting, December 28, 1893.

this yellow precipitate in a specially graduated apparatus. Perhaps however, by far the largest number of chemists, prefer to treat the yellow precipitate by some volumetric method, either what may be called the alkali method, described by Handy in the *Proceedings of the Engineer's Society of Western Penna.*, 8, 78, or the perhaps better known permanganate method, described by Emmerton, published in the *Trans. A. I. M. E.*, 15, 93, and subsequently modified by Wood, Shimer, Drown, Jones, and others. We use the permanganate method. This method as we prefer to use it, and with all the precautions which we deem essential to secure uniform and accurate results, except as to the interference produced by arsenic, has been published in the *J. Anal. Appl. Chem.*, 7, 108, and also in the *J. Am. Chem. Soc.* 15, 519. What follows is a discussion of some points suggested by the work done preliminary to drawing up the method above referred to.

In order that what is given may be clearly understood, it may not be amiss to state that by this method, the steel is dissolved in nitric acid of 1.13 sp. gr., the solution boiled a few seconds, and then treated with potassium permanganate to destroy carbonaceous matter, and possibly secure complete oxidation of the phosphorus; the separated manganese oxide, reduced by a few crumbs of ferrous sulphate, the solution then heated to a definite temperature, and a measured volume of molybdate solution, which is likewise at a definite temperature, added, the vessel enclosed to prevent loss of heat, and shaken vigorously for five minutes, allowed to stand a few minutes for the precipitate to settle, and then filtered. After thorough washing with acid ammonium sulphate wash water, the yellow precipitate is dissolved in ammonia, the solution treated with a definite amount of sulphuric acid, and then passed through the reductor, and finally titrated with potassium permanganate of known strength, the amount of phosphorus being ultimately obtained by multiplying the number of cubic centimeters of permanganate used by the proper factor.

It is obvious that the accuracy of the determination by the method briefly outlined above, depends on several conditions:

- I. Is all the phosphorus in the steel taken to start with

actually in the yellow precipitate obtained, or in other words, can phosphorus be completely separated from iron by molybdic acid? Upon this point we have done no work, and cannot express an opinion. The late J. Lawrence Smith used to claim that the complete separation of very small amounts of phosphorus from large amounts of iron by means of molybdic acid was at least doubtful, and that the most reliable procedure consisted in first concentrating the phosphorus into a very small amount of iron, and then separating it from this iron by means of molybdic acid. Assuming, however, that all the phosphorus in the steel is in the yellow precipitate, several further questions arise.

II. Is the yellow precipitate of constant composition, that is, is it independent of the conditions under which it is formed? It is obvious that this is a very important point for all those methods which either weigh or measure the yellow precipitate, and also for the permanganate volumetric method, which in reality actually measures not the phosphorus or phosphoric acid in the yellow precipitate but rather the molybdic acid, the phosphorus being determined from its relation to the molybdic acid. If now the yellow precipitate is not of constant composition, or more definitely if the relation between the phosphorus and molybdic acid in this precipitate is not a constant one, but is affected by the conditions under which the precipitate is formed, it is clear that these conditions must be definitely defined, and always closely followed, or there will be great uncertainty in the results. What then are the facts in the case? It is well known that almost from the beginning of the use of molybdic acid in phosphorus determinations there has been more or less uncertainty as to the constitution of the yellow precipitate, and especially that, depending on the conditions, it is very liable to be contaminated with free molybdic acid. Furthermore, Emmerton has apparently demonstrated in the place cited above, that the temperature of precipitation has a very important influence on the final result. He also claims that the amount of free acid in the solution, the concentration of the solution, and the length of time allowed for precipitation also affect the final result. Other workers, especially Wood, in the

*J. Anal. Chem.*, **1**, 138, Shimer, *Trans. A. I. M. E.*, **17**, 100, and Drown, *Trans. A. I. M. E.*, **18**, 90, have put a good deal of study on the method. None of the determinations given that we have been able to study, show that the final result is independent of the conditions under which the yellow precipitate is obtained. We ourselves have made a good many experiments, varying the conditions under which the yellow precipitate is obtained, and feel safe in saying that almost any variation in the conditions will produce some difference in the final result. Much of our work simply confirms that of other operators. Perhaps it would be worth while to give a single illustration.

Two sets of one gram each of three samples of steel containing different amounts of carbon and phosphorus were dissolved in seventy-five cc. of 1.13 sp. gr. nitric acid, and further treated exactly alike according to our standard method above referred to, except that before adding the molybdate solution, ten cc. of strong ammonia was added to each flask of one set. This procedure would as is evident, result in the formation of the yellow precipitate in one set in a menstruum containing more ammonium nitrate, and less free nitric acid than the other contained. The results obtained are as follows, the figures being the phosphorus in the three steels:

		No. 1 steel.	No. 2 steel.	No. 3 steel.
		Per cent.	Per cent.	Per cent.
Without ammonia	1 .....	0.036	0.055	0.029
	2 .....	0.037	0.055	0.029
	3 .....	0.037	0.055	0.030
With ammonia ...	1 .....	0.047	0.064	0.036
	2 .....	0.043	0.062	0.033
	3 .....	0.045	0.067	0.039

The difference in the results is quite marked. Diminution in free acid and increase in ammonium nitrate apparently leads to higher figures and less uniformity in duplicate determinations. Some of our experiments indicate that even a much less change in the proportions of free acid and ammonium nitrate than given above affects the final result. Also that in addition to the variables mentioned above, a different result is obtained when sugar or other organic substance is used to reduce the separated manganese oxide than is given when ferrous sulphate

is used. Finally there are quite strong indications, that the total amount of molybdic acid present in the solution and even its state of oxidation have an influence on the final figures obtained.

If it be allowed then that the conditions, under which the yellow precipitate is formed affect its constitution, or more definitely, affect the ratio between the molybdenum and phosphorus in this precipitate, or what amounts to the same thing, affect the final result, two things are evident.

1. In order to secure accurate and concordant results, it is necessary that the conditions under which the yellow precipitate is obtained shall be very clearly and sharply defined, and that on making the analyses, these conditions shall be very rigidly maintained.

2. It will not do to use ratios based on the analysis of the yellow precipitate obtained under one set of conditions as a means of calculation for precipitates obtained under another and different set of conditions.

As an example of this second statement, it seems clear, if the preceding views are correct, that if a chemist obtains a quantity of the yellow precipitate from sodium phosphate with no iron present, and the conditions entirely different from those which prevail in the determination of phosphorus in steel, and then makes an analysis of this yellow precipitate to determine the ratio between molybdic acid and phosphorus, although the figures he obtains may be quite accurate, he is still not at liberty to use these figures in determining phosphorus in iron and steel and claim that they give accurate results. It is of course conceded that they may be accurate but there is no certainty of this. It should be stated that the amount of phosphorus in the yellow precipitate is so small, and the amount of molybdic acid is so large, that there is room for considerable variation in ratios without giving rise to very serious differences in results, especially in steels low in phosphorus. This fact may help to account for the claim so generally made by different chemists that their results agree within reasonable limits of error with those of other good chemists. But if it is desired to obtain fairly accurate and concordant results, we see no way of escaping from the two statements given above.

If these points be conceded it is obvious that a still further very important question arises, *viz.*:

III. How shall the proper factor for use with the permanganate of potash be obtained? It is clear, since the permanganate of potash solution is standardized against metallic iron, that we need two ratios, first, the ratio between molybdic acid and iron, and second, the ratio between molybdic acid and phosphorus in the yellow precipitate obtained under definite conditions. What then are these ratios? On looking over the literature on the subject, we find two or three serious uncertainties. The ratio between iron and molybdic acid is evidently affected by the change which takes place in the molybdic acid when it passes through the reductor, and we do not find that there is agreement between those who have worked on this point. Furthermore, Jones has apparently shown in the *Trans. A. I. M. E.*, 18, 705, that the use of the reductor gives different results than are obtained when the molybdic acid in the yellow precipitate is reduced by granulated zinc in a beaker as originally proposed by Emmerton. Again the published ratios between molybdic acid and phosphorus, vary between 100 : 1.54 and 100 : 1.90 if we may use our own figures for illustration. It is clear therefore that there are two difficulties in the way of using any of the published ratios, first, which ratios shall be used, and second, the point already discussed quite at length, that these ratios vary, or at least the final results vary according to the conditions under which the yellow precipitate is obtained.

Two methods of procedure are clearly open to us.

First, obtain a quantity of the yellow precipitate under the conditions which we deem essential, and then make independent determinations of the phosphorus and molybdic acid in this precipitate. This would give the ratio between these two constituents. Then pass a quantity of the same precipitate through the reductor and titrate with permanganate. This will give the ratio between molybdic acid and iron. This we have not done yet, partly for lack of time and partly from the difficulties of the analysis. In our experience it is not easy to dry and weigh the yellow precipitate without its undergoing change in the process, and our experience with methods of determining

molybdcic acid is also meager. There is need of some good and careful work on this point.

In view of these uncertainties, we chose the other method of procedure, *viz.*:

Second, determine the phosphorus in several samples of steel by the most accurate known gravimetric method, then make an analysis for phosphorus in these same steels by the volumetric method, and then use such a factor with the potassium permanganate as will bring these results together. The work done on the steels chosen for this purpose is given in our paper "On an Attempt to Find the Amount of Phosphorus in Three Samples of Steel."

It is evident that this procedure, while it enables us to get a factor to use with the potassium permanganate in the phosphorus determinations by the volumetric method as we use it, does not throw any light on the ratios between iron and molybdcic acid, and between molybdcic acid and phosphorus in the yellow precipitate as we obtain it. But if we assume that the ratio of iron to molybdcic acid is 100 : 90.76 it follows that the ratio of molybdcic acid to phosphorus in the yellow precipitate as we obtain it is 100 : 1.90 and this is the calculation which we have used in our published volumetric method above referred to.

One further question may arise, *viz.*: In view of the apparent variability of the yellow precipitate according to the conditions under which it is obtained,

IV. If the conditions are made constant, will the results obtained be uniform and agree with each other?

In reply to this we may say that so far as our experience has gone, the agreement between duplicate determinations on the same sample of steel where the conditions of the method as published are rigidly adhered to, rarely exceeds more than a couple of thousandths of a per cent., also different operators using the published method on the same sample of steel, after a little experience is obtained with it, rarely disagree more than three or four thousandths.



# THE EXACT DETERMINATION OF PHOSPHORUS BY THE MOLYBDATE METHOD IN IRON, STEEL, AND ORES, WHICH CONTAIN ARSENIC.<sup>1</sup>

BY JAMES O. HANDY, Chemist of The Pittsburgh Testing Laboratory, L't'd.

## CLASSIFICATION OF EXISTING METHODS FOR PHOSPHORUS.

1. The acetate method of Blair and others.
2. The molybdate methods.
  - (a) Methods in which the phosphomolybdate is weighed (methods of E. F. Wood and others).
  - (b) Methods in which the amount of yellow precipitate is estimated volumetrically.
    - (a') By permanganate (methods of Emmerton, Drown, Jones, and others).
    - (b') By alkali (methods of Manby, Handy, and others).
3. The combination methods.
  - (a) The acetate and molybdate methods.
  - (b) The molybdate and magnesia methods.

In the "acetate" methods the phosphorus is precipitated as phosphate, after separating by hydrogen sulphide, any arsenic which is present. The methods are long and the manipulation difficult.

In the "molybdate" methods, the phosphorus is precipitated as ammonium phosphomolybdate and weighed or titrated. Arsenic, which is believed to be of rare occurrence, is disregarded. It is, however, a fact, that, when arsenic is present in a solution from which phosphorus is precipitated as phosphomolybdate, a portion of the arsenic accompanies and contaminates the phosphorus precipitate.

The "molybdate" methods are in general, very short and their manipulation simple; they are widely used. With the drawback of arsenic interference removed, the molybdate method takes front rank for simplicity, brevity and accuracy.

<sup>1</sup> Read at the Baltimore meeting, December 28, 1893.

TABLE I.  
EXTENT OF THE INTERFERENCE OF ARSENIC IN PHOSPHORUS  
DETERMINATIONS.

Substance analyzed.	Phosphorus per cent. contained.	Arsenic per cent. contained.	Method.	Temperature of precipitation.	Apparent per cent. phosphorus.	Error caused by arsenic.	Remarks.
Steel	0.096	0.050	J. O. Handy	85° C.	0.094	None	Within
"	0.096	0.050	"	"	0.095	"	limit of error
"	0.098	0.100	"	"	0.098	"	"
"	0.098	0.100	"	"	0.099	" to 0.001	"
"	0.096	0.250	"	"	0.099	0.003	"
"	0.096	0.350	"	"	0.102	0.006	"
"	0.096	0.500	"	"	0.106	0.010	"
"	0.096	0.750	"	"	0.111	0.015	"
"	0.096	1.870	"	"	0.125	0.029	"
"	0.012	0.100	"	"	0.012	"	"
"	0.012	0.500	"	"	0.011	"	"
"	0.012	1.000	"	"	0.011	"	"
Pig iron	0.036	0.100	"	"	0.039	0.003	"
"	0.036	0.150	"	"	0.043	0.007	"
"	0.083	0.100	"	"	0.088	0.005	"
"	0.083	0.150	"	"	0.094	0.011	"
"	0.297	0.500	{ and we'h'g }	"	0.315	0.018	"
Ferro-mang'se	0.292	0.500	{ evaporat'n neutraliz'n weighing }	"	0.313	0.021	"
Iron ore	0.096	0.500	"	"	0.135	0.038	"
Mang'se ore	0.212	0.500	"	"	0.264	0.052	"

EXPERIMENTS PROVING THAT ARSENIC DOES NOT PRECIPITATE WHEN LITTLE OR NO PHOSPHORUS IS PRESENT.

*Experiments.*—Two grams of magnetic iron ore, (a very pure concentrate), showed 0.002 per cent. phosphorus. A duplicate containing 0.500 per cent. of arsenic, in the fully oxidized form, showed also exactly 0.002 per cent. of phosphorus.

The filtrate, which contained arsenic, was heated for a short time to 60°–70° C. before molybdic acid or arsenomolybdate began to separate. The same result was repeatedly obtained with arsenical filtrates from phosphomolybdate precipitates.

A solution of arsenic acid in nitric acid, properly prepared as for phosphorus determination gives no precipitate at 85° C. with molybdate solution unless the heating is continued.

The experiments described prove very clearly that the precipitation of arsenic with phosphomolybdate is a mechanical one; that the arsenic is only *dragged* down. With little or no phosphorus, no arsenic precipitates.

The case is parallel to the contamination of the first ferric

hydroxide precipitate, with lime, or of the first oxalate of lime precipitate, with magnesia.

In these cases, solution and re-precipitation of the contaminated precipitates, effects their purification.

Experiments (Table II) prove that the same treatment, properly applied, is equally efficient in purifying arsenical phosphomolybdate.

The exact method of procedure follows :

TABLE II.  
ELIMINATION OF ARSENIC FROM PHOSPHOMOLYBDATE.

Substance analyzed.	Phosphorus contained.	Arsenic contained.	Method.	Temperature of precipitation.		Phosphorus found.	Error.
				First	Second		
Steel	0.096	0.500	J. O. Handy	80° C.	75° C.	0.096	none
"	0.096	0.500	"	"	"	0.096	"
"	0.096	0.500	"	"	"	0.097	0.001
"	0.096	1.000	"	"	"	0.097	0.001
"	0.096	none	"	"	"	0.095	0.001
"	0.096	"	"	"	"	0.095	0.001
"	0.096	"	"	"	"	0.094	0.002
"	0.096	0.500	"	85° C.	85° C.	0.097	0.001
"	0.096	0.500	"	"	80° C.	0.094	0.002
"	0.038	0.500	"	80° C.	75° C.	0.036	0.002
"	0.038	0.500	"	"	"	0.037	0.001
"	0.038	0.500	"	"	"	0.039	0.001
"	0.038	none	"	"	"	0.037	0.001
Pig iron	0.082	0.500	"	"	"	0.081	0.001
"	0.082	0.500	"	"	"	0.081	0.001
Ferro-mang'se	0.282	0.500	{ evaporat'g } { weighing }	85° C.	75° C.	0.281	0.001
Pig iron	0.286*	0.500	J. O. H. and "	"	"	0.289	0.003*
Iron ore	0.083	0.500	Evap. " "	"	"	0.085	0.002
Manganese	0.199	0.500	"	"	"	0.200	0.001

\* NOTE.—A little lost.

#### THE METHOD OF REDISSOLVING THE PHOSPHOMOLYBDATE AND FREEING IT FROM ARSENIC.

Having separated the phosphorus as phosphomolybdate by any good method and washed it well with one per cent. nitric acid, place a twelve ounce Erlenmeyer flask under the funnel.

Dissolve the yellow precipitate by ammonium hydroxide wash (1 : 6), using about fifteen cc. in all, and wash it into the flask. Dilute the solution to about seventy-five cc. and heat to 75° C. and add a mixture of ten cc. HNO<sub>3</sub> (1.42) and twenty-five cc. of molybdate solution (E. F. Wood's formula), shake well, filter and wash

- (a) with one per cent. nitric acid, dry and weigh, or  
(b) with one per cent. nitric acid and  $\frac{1}{10}$  per cent. potassium nitrate, dissolve and titrate (Handy's method).

The greater part of the analytical work of this paper has been done by my assistant Mr. Geo. O. Loeffler.

#### METHODS USED.

*For Steel and Pig-iron.*—The method used in all analyses of steel and pig-iron, was the one published by the author in 1892 (*Trans. Engineer's Society of Western Pennsylvania* March, 1892, and *J. Anal. Appl. Chem.*, April, 1892).

*For Ferromanganese.*—Two grams, dissolved in nitric acid, (1.42), and the solution evaporated to dryness. The residue, having been redissolved in hydrochloric acid, (1.20) the solution was diluted and filtered. The filtrate was treated with ammonium hydroxide till ammoniacal, then acidified with nitric acid, heated to 85° C. and precipitated with fifty cc. of molybdate solution.

*For Iron and Manganese Ores.*—Two grams dissolved in aqua regia (five per cent.  $\text{HNO}_3$ , (1.42) and ninety-five per cent.  $\text{HCl}$  (1.20), and the solution evaporated to dryness. Subsequent procedure was as described above for ferromanganese after the evaporation. Phosphorus, in "insoluble residues" was separated and determined.

*Arsenic* was added as dry  $\text{As}_2\text{O}_3$  to the samples when weighed out. The reagents used in the analysis oxidized it to arsenic oxide.

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### NOTES AND QUERIES ON DR. DUDLEY'S METHOD OF DETERMINING PHOSPHORUS IN STEEL.

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THE object of the work outlined in this paper was to ascertain the accuracy of the method proposed by Dr. Dudley for the volumetric analysis of phosphorus in steel, described in *J. Am. Chem. Soc.*, Sept., 1893, p. 519, and to determine if a separation of phosphorus could be made in the presence of arsenic with a sufficient degree of accuracy for commercial purposes

by this method or any modification of it.

Our first undertaking was to ascertain if the new ratio between phosphorus and molybdic acid in the yellow precipitate of 1.90, brought forward by Dr. Dudley, was correct. The commonly accepted factor as found by Emmerton and others is 1.794, *Trans. A. I. M. E.*, **15**, 93, R. Finkener, *Ber. d. chem. Ges.*, **11**, 1638, Henry Pemberton, *Chem. News*, **46**, 4, Von der Pfordten, *Ztschr. anal. Chem.*, **23**, 422, and very recent work by H. C. Babbitt, *J. Anal. Appl. Chem.*, **7**, 165, has confirmed this ratio. However, as Dr. Dudley used an entirely different method for determining this ratio, we have followed as nearly as possible his work as outlined in the *American Engineer and Railroad Journal*, Jan. 1893, p. 18, but have been wholly unable to obtain his figure.

*Determination of the Ratio between Phosphorus and Molybdic Acid in the Yellow Precipitate.*—Four samples of steel of very different carbon composition were taken, and the phosphorus determined both gravimetrically and volumetrically in each, and from the figures obtained, the ratio between the phosphorus and the molybdic acid in the yellow precipitate, formed in the volumetric analysis under the conditions used, was computed. The complete analyses of the steel used in this and subsequent investigations are as follows:

	Carbon, per cent.	Manganese, per cent.	Silicon, per cent.	Gravimetric phosphorus, per cent.	Sulphur, per cent.
No. 27....	0.188	0.321	0.020	0.110	0.052
No. 789....	0.997	0.427	0.226	0.021	0.024
No. 344....	0.588	1.295	0.079	0.065	0.107
No. 65....	0.166	0.577	0.072	0.012	0.025

For our gravimetric determination we used the combination method as described by Dr. Dudley. The acetate method was followed up to the point of obtaining the basic acetate precipitate, at which stage enough bromine water was added to oxidize fully one-half a gram of iron, and the solution boiled. It was then cooled down and the acetate precipitation made exactly as described in Chemical Analysis of Iron, by A. A. Blair. This precipitate was dissolved in hydrochloric acid, and all traces of iron washed from the paper. After expelling the hydrochloric acid from the filtrate by repeated evaporations with nitric acid, seventy-five cc. of nitric acid 1.135 sp. gr. were added, the solu-

tion boiled, oxidized with potassium permanganate, and reduced with ferrous sulphate, as described in Dr. Dudley's routine method. The solution at 85° C. was then treated with seventy-five cc. of molybdic acid at 27° C., the yellow precipitate shaken down, filtered and washed free of molybdic acid. We test for the presence of molybdic acid as follows: About four cc. of the acid wash water are caught in a test tube as they run through the filter, and treated with a few drops of dilute ammonium sulphide. The least presence of molybdic acid will cause the liquid to darken slightly. The cloud of sulphur produced by the addition of ammonium sulphide to the acid solution does not interfere in any way with the delicacy of the test. We have found this test far more sensitive than the one used by Dr. Dudley, who allows the acid wash water to drop into a dilute solution of ammonium sulphide, the test thus being in the alkaline solution. We have frequently found yellow precipitates which according to the alkaline solution test were thoroughly washed, yet with the acid test show unmistakable signs of molybdic acid which required one or two more washings to remove. The yellow precipitate was then dissolved in ammonia and saturated while warm with hydrogen sulphide, and the red solution of molybdenum sulphide slightly acidified with hydrochloric acid. The precipitate of molybdenum sulphide was allowed to settle, then filtered off rapidly on a large folded filter, avoiding contact with the air as much as possible, and washed thoroughly with strong hydrogen sulphide water containing a little hydrochloric acid. The large filtrate was then evaporated, and on boiling, it was invariably found that a small amount of molybdenum sulphide separated out. This was filtered off and the resulting filtrate concentrated to a bulk of about four cc. The phosphorus was then precipitated with from five to eight cc. of magnesia mixture and a small amount of ammonium hydroxide, the cold solution being vigorously stirred until precipitation began, when ammonium hydroxide amounting to one-third of the bulk of the solution was added, and the analysis allowed to stand for twelve hours. The precipitate was then filtered off, washed with ammonium nitrate until free from chlorine, and ignited. This precipitate was invariably contaminated with molybdic acid. It

was purified by dissolving in hot dilute hydrochloric acid, filtering, evaporating the filtrate to a small bulk, and precipitating as before. For our volumetric determination of the phosphorus in these samples we followed the preceding method up to the point of obtaining the ammoniacal solution of the yellow precipitate. This solution was acidified with sulphuric acid, passed through the reductor and titrated with permanganate, one cc. of which equals 0.003350 grams iron, and assuming as Dr. Dudley has, that the ratio between iron and molybdic acid is 90.76, the commonly accepted factor, we obtain the results in the table below.

No.	Permanganate used by volumet- ric method, cubic centimeters.	Phosphorus by gravimetric method, per cent.	Ratio between phosphorus and molybdic acid.	Error in ratio for each 0.001 per cent. error in gravimetric determination.
27....	103.1	0.110	1 : 1.759	0.016
" 789....	19.0	0.021	1 : 1.826	0.087
" 344....	59.4	0.065	1 : 1.813	0.027
" 65....	11.2	0.012	1 : 1.806	0.151

A glance at the ratios obtained between phosphorus and molybdic acid in the above table will show that they are very irregular, but this will be explained by the last column of figures which point out that the gravimetric determinations of phosphorus must be made with absolute accuracy in order to have these ratios agree. The only point we wish to call attention to in the above table of ratios is the fact that they are all much lower than the ratio 1.90 proposed by Dr. Dudley, and obtained by him in a similar manner.

Not satisfied with the above results, we turned our attention to the actual analysis of the yellow precipitate, which was prepared for our investigations as follows: To a solution of ferric nitrate in nitric acid of 1.135 sp. gr., was added a sufficient amount of phosphoric acid to make the solution correspond to that of a steel containing about one per cent. of phosphorus. The yellow precipitate was shaken down from this, exactly in accordance with Dr. Dudley's method of phosphorus analysis. It was washed by decantation with ammonium sulphate, then with water, and finally dried to a constant weight at 130° C. This precipitate was found to be so hygroscopic that it was practically impossible to obtain accurate weights of it for analy-

sis. To avoid this difficulty, after carefully weighing it, the entire precipitate was dissolved in a slight excess of ammonium hydroxide, filtered through a balanced filter paper into a tared 200 cc. flask, the filter being washed with water until the 200 cc. mark was reached. The small amount of insoluble matter on the filter was determined after drying at  $100^{\circ}$  C., and the weight deducted from the original weight of the yellow precipitate. We now have a known weight of yellow precipitate in a known weight of solution, successive portions of which were weighed out from time to time for the determination of phosphorus and molybdic acid.

*Phosphorus in Yellow Precipitate.*—This was determined as follows: Accurately weigh off about twenty-five grams of solution, which is equivalent to about one gram of yellow precipitate, add ten cc. of magnesia mixture, stir well until precipitation begins, then add ammonium hydroxide to the amount of about one-third the bulk of the original solution, and allow to stand for several hours. Filter and wash with ammonium nitrate solution until free from chlorine, then ignite while moist. Purify the magnesium pyrophosphate by dissolving in dilute hydrochloric acid, filtering from any insoluble residue, and precipitating as before by the addition of ammonium hydroxide, five cc. of ammonium chloride solution, and five cc. of magnesium mixture. Allow to stand twelve hours, ignite and weigh.

The reagents used were made up as follows:

Ammonium chloride.—One part ammonium chloride to eight parts of water.

Magnesia mixture.—From magnesium chloride as per Chemical Analysis of Iron, p. 58, by A. A. Blair.

Ammonium hydroxide.—0.90 sp. gr.

Ammonium nitrate wash water.—One part ammonium hydroxide 0.90 sp. gr. to three parts water, then add two grams of ammonium nitrate for each 100 cc. of solution.

*Molybdic Acid in Yellow Precipitate.*—The method used for this determination was as follows: Weigh off accurately an amount of solution equivalent to about 0.25 gram of yellow precipitate, dilute with 150 cc. of water and bring to a boil. Neutralize the boiling solution with acetic acid, and add about five cc. in excess of the neutral point. Add at once twenty-five cc. of lead acetate,



or one cc. for every 0.01 gram of yellow precipitate present in the solution, and allow to digest an hour and a half at nearly a boiling temperature, in order to render the precipitate compact and granular. Filter on a Gooch crucible and wash with hot water about eight times by decantation. After the fifth or sixth washing the filtrate should give no reaction for lead when tested with ammonium sulphide. Dry to a constant weight at  $130^{\circ}\text{C}$ . This gives us the weight of  $\text{Pb}_3(\text{PO}_4)_2 + \text{PbMoO}_4$ . From the previous determination of phosphorus we now compute the  $\text{Pb}_3(\text{PO}_4)_2$ , and deduct this weight from that of the mixed precipitates. The difference gives us the weight of  $\text{PbMoO}_4$ , which multiplied by the factor 0.39237 equals molybdic acid ( $\text{MoO}_3$ ).

The reagents used were made up as follows:

*Lead Acetate*.—Sixty grams crystallized salt in two liters of water, to which fifteen cc. of acetic acid were added.

*Acetic Acid*.—1.04 specific gravity.

Before using the above method for the determination of molybdic acid, we carefully investigated its merits and found it to be thoroughly reliable under all ordinary conditions of precipitation, the acidity, bulk and temperature of the solution having only a slight influence. On attempting to ignite the precipitate, however, as directed in the method as originally published in the *Ber. d. chem. Ges.*, 4, 280, we invariably found a loss varying from 0.2 per cent. to 3.0 per cent., and even more, according to the duration and intensity of ignition. But by drying on a Gooch crucible at  $130^{\circ}\text{C}$ . we obtained very constant results, which we believe to be in every way reliable.

The analysis of the yellow precipitate by the above methods gave us as follows: Phosphorus, 1.648 and 1.644 per cent., an average of 1.646 per cent.

Molybdic acid, 91.61, 91.59, 91.61 and 91.57 per cent., an average of 91.595 per cent. Our ratio between phosphorus and molybdic acid as computed on these analyses is 1.797.

We determined the molybdic acid in the filtrates from the phosphorus determinations and obtained 92.25 and 92.41 per cent. These results are higher than those previously obtained in the separate determinations, but as this difference was not sufficient to change to any extent our ratio we did not investigate the cause.

We now went a step further, in order to prove that the ratio between the phosphorus and molybdic acid in the yellow precipitate actually obtained in a steel analysis, is identically the same as that in the yellow precipitate shaken down from the prepared solution of phosphorus.

We separated a considerable amount of yellow precipitate from a steel containing 0.10 per cent. phosphorus, by Dr. Dudley's method of analysis, and after drying to a constant weight at 130° C. made the determinations of phosphorus and molybdic acid exactly as in the case of the previous precipitate, obtaining the following results: Phosphorus, 1.638 and 1.648 per cent., an average of 1.643 per cent. Molybdic acid, 91.63 and 91.67 per cent., an average of 91.65 per cent.

The ratio between phosphorus and molybdic acid given by these figures is 1.792, thus confirming our previous results and the generally accepted figure of 1.794.

From the work above outlined it would seem evident that the ratio of phosphorus to molybdic acid can be derived much more accurately from the analysis of the yellow precipitate than by the method suggested by Dr. Dudley.

The elaborate investigations of Hundeschagen (*Chem. News*, Oct. 4, 11, 18, 25, and Nov. 1, 1889,) have shown that ammonium phosphomolybdate is far more uniform when prepared under varying conditions than was formerly supposed. If the conditions of precipitation of the yellow precipitate are maintained constant, there is but little doubt as to its uniform composition. The ratio then becomes a question of the accuracy of the determinations of phosphorus and molybdic acid in the yellow precipitate. We have accordingly given the methods used for these determinations as completely as possible, in order to afford an opportunity for criticism and duplication.

*Ratio between Iron and Molybdic Acid.*—The ratio between phosphorus and molybdic acid being established, we then took up the ratio between iron and molybdic acid, as the investigations of Mr. Babbitt, *J. Anal. Appl. Chem.*, 7, 165, and our own experience had indicated that the commonly accepted ratio, 90.76, is too high where the reductor is used, the reduction being considerably greater than with the ordinary method of reducing with zinc powder and shot.

Our first experiments were on the standardization of a permanganate solution by the ordinary method of dissolving the steel in a flask in an atmosphere of carbon dioxide gas, as compared with the figure obtained when the steel was dissolved in an open beaker and reduced through the reductor. No appreciable difference was found, the reduction being complete in both cases.

We then made a large solution of molybdic acid of such a strength that fifty cc. contained 0.25 gram of the salt. The first experiments with this solution were made after the reductor had been in use some time, and the zinc was packed closely together, so that the solution encountered considerable resistance to its progress, and the acid had some time to act on the zinc, the result being that the reductor became quite hot. Upon cleaning out the reductor and filling with entirely fresh zinc, we were surprised to find our results very appreciably lower, no matter how slowly the solution was passed through the reductor, and only after heating the solution nearly to boiling did we obtain the results in the first case. This demonstrates that care must be taken to have the solutions hot when they are reduced, in order to obtain complete reduction, but with this precaution the results are very uniform, as will be seen from the table following. In each of the following experiments fifty cc. of the above mentioned molybdic acid solution was used.

Experiments with reductor:

RESULTS EXPRESSED IN CUBIC CENTIMETERS OF PERMANGANATE.

REDUCTOR CLOGGED FROM LONG USE.		REDUCTOR CONTAINING FRESH ZINC.		
Five cc. sulphuric acid, cubic centimeters.	Ten cc. sulphuric acid, cubic centimeters.	Five cc. sulphuric acid, cubic centimeters.	Ten cc. sulphuric acid, cubic centimeters.	Five cc. sulphuric acid solution heated to 95° C., cubic centimeters.
....	75.2	74.8	74.6	....
75.25	75.3	75.0	74.7	75.45
75.35	75.4	74.9	74.7	75.35
75.45	75.3	74.95	74.8	75.35
Average, 75.35		74.91	74.70	75.38

Our experience with the reductor has been that in order to secure complete reduction, it is necessary to have the column of zinc of considerable length, and to pass the solution through

very slowly. We would not feel safe in using a column of zinc less than ten inches in length. In reducing a solution which has a bulk of 200 cc. at least two minutes should be allowed for passing through.

Turning now to the reduction of molybdic acid by heating with zinc and sulphuric acid, we found that very different results could be obtained by the various modifications of the method. These methods vary not only in the amounts of zinc and sulphuric acid recommended, but also in the temperature used and the time of heating.

We experimented with the method given in Chemical Analysis of Iron, by A. A. Blair, p. 97. Fifty cc. of our stock molybdate solution reduced in this manner required 73.23 cc. of permanganate.

We then reduced the molybdic acid solution as follows: Fifty cc. of stock molybdic acid were measured off, twenty grams of zinc (and four large shot) were added, together with thirty cc. of ammonia (1:3). This was heated almost to boiling, eighty cc. of hot sulphuric acid (1:4) added, and allowed to reduce for fifteen minutes, keeping the solution at a gentle boil. Fifty cc. of the stock solution reduced in this manner gave as a mean of a number of determinations 74.2 cc. of permanganate.

It will be noticed that there is quite a difference between these results, and also that the highest value obtained by the zinc and sulphuric acid method is considerably lower than that given by the reductor. In some laboratories the zinc and sulphuric acid method of reduction is used with a less amount of zinc, shorter time, and at temperatures which do not reach the boiling point. In such cases the reduction is certainly far from complete.

The mean of four gravimetric determinations upon this same solution show the amount of molybdic acid contained in fifty cc. to be 0.233264 gram. The average number of cubic centimeters of permanganate used in titrating this amount after being passed through the reductor is 75.35, hence one cc. permanganate = 0.003096 molybdic acid. A careful standardization of the permanganate solution against iron gave its value as one cc. = 0.003472 gram iron, hence the ratio between iron and molybdic

acid, when the reduction is made by means of the reductor in our hands gives 89.16 instead of 90.76 as found by Mr. Emmerton. This difference is readily accounted for by the difference in the method of reducing the solutions. Our figure tends to corroborate the work of Mr. Babbitt in this connection although it does not correspond exactly with the one he obtained. From the foregoing work it would seem that the ratio between phosphorus and molybdic acid of 1.794 is correct, but that where the reductor is used 89.16 represents more nearly the correct ratio between iron and molybdic acid, hence our results are computed on this basis.

*The Effect of Temperature on the Precipitation of Arsenic.*—With the exception of these factors we found no fault with the method given by Dr. Dudley and the uniformity of the results obtained was very gratifying. To divide the errors liable to occur in weighing out the sample, and for convenience in manipulation, we have altered the method slightly in the direction of using a larger sample of steel and smaller bulk of solutions. A large number of determinations have proved that we do not in any way decrease the accuracy of our results by these changes. In detail, the method, as used by us, is as follows: Dissolve 1.5 grams steel in seventy-five cc. nitric acid 1.135 sp. gr. in an eight-ounce Erlenmeyer flask, allow to dissolve on the hot plate and boil hard for about one minute after the steel is in complete solution. Add crystals of potassium permanganate until a permanent purple color is obtained which will remain for at least one-half a minute on boiling. In order to secure such a color, enough permanganate must be added to form a copious dark brown precipitate of manganese dioxide. The crystals of permanganate must be added carefully to prevent the solution from boiling over. Remove the flask from the plate and add ferrous sulphate free from phosphorus, with constant shaking, until the solution clears. Cool to 38° C. and add seventy-five cc. molybdic acid at 27° C. Shake hard for five minutes, filter off the yellow precipitate and wash with ammonium sulphate wash water until the filtrate shows no reaction for molybdic acid when tested as previously described. Dissolve the precipitate in ammonia (1:3), using as little as possible. Wash the paper once with water, and pass the liquid back through the filter and wash

thoroughly. The bulk of this filtrate should not exceed 150 cc. Acidify with five cc. concentrated sulphuric acid, and reduce with the aid of the reductor, passing the liquid slowly through a ten-inch column of zinc. Titrate with potassium permanganate.

Our next step was to ascertain if the method or any modification of it could be used in the presence of arsenic without serious error from that source. Solutions of arsenic were made up by dissolving arsenious oxide in a small amount of a solution of sodium acid carbonate, and diluting with nitric acid 1.135 sp. gr. The strength of these solutions was so adjusted that seventy-five cc. of each would correspond to 0.1, 0.5, and 1 per cent. of arsenic when 1.5 grams of steel are used. Blank experiments were first made with the chemicals to be used, following in every detail the method given. The average of the results obtained are given in the table which follows. We then shook down in the same manner the three arsenic solutions prepared as stated, trying the effect of different temperatures, but were unable to bring down any appreciable amount of arsenic as the table will show.

	Percentage of arsenic added.	Temperature of solution.	Temperature of molybdic acid.	Temperature of the mixture when shaken.	Result in terms of phosphorus, per cent.	Blank exper. on chemicals in terms of phosphorus, per cent.	Arsenic obtained in terms of phosphorus, per cent.
Blank exper.	..	85° C.	27° C.	52° C.	.....	0.0006	.....
Blank exper.	..	16°	16°	16°	.....	0.00034	.....
Blank exper. plus arsenic.	1	85°	27°	52°	0.0023	.....	0.0017
"	1	16°	16°	16°	0.0010	.....	0.0066
"	5	85°	27°	52°	0.00085	.....	0.0051
"	5	27°	27°	27°	0.0016	.....	0.0010
"	1	85°	27°	52°	0.0018	.....	0.0012
"	1	16°	16°	16°	0.0014	.....	0.0011
"	5	85°	27°	52°	0.0014	.....	0.0011
"	5	27°	27°	27°	0.0018	.....	0.0012
"	1	85°	27°	52°	0.0018	.....	0.0012
"	1	16°	16°	16°	0.0018	.....	0.0015
"	5	85°	27°	52°	0.0018	.....	0.0015

These tabulated results gave us no little surprise, being so entirely contrary to the behavior usually attributed to arsenic. But we have repeatedly duplicated them, confirming our first results in every case. To investigate the matter still further we made a solution of pure nitrate of iron and phosphoric acid of such a strength that twenty cc. contained approximately 1.5 grams of iron and one-half per cent. of phosphorus. Analysis of

this solution, made as before and shaken down at 85° C., gave 0.442 per cent. phosphorus, duplicate 0.446 per cent. On the addition of 0.25 per cent. of arsenic to this solution and shaking down at 85° we obtained 0.484 per cent. phosphorus, duplicate 0.489 per cent., or an increase of 0.4 per cent., due to the arsenic added. We then took the four samples of steel on which our previous work had been done, and to each of these was added 0.1 per cent. of arsenic and the analysis shaken down with the results shown in the following table:

	Arsenic added, per cent.	Temperature of solution.	Temperature of molybdic acid.	Temperature of mixture when shaken.	Phosphorus obtained before arsenic was added.	Phosphorus obtained after arsenic was added.	Arsenic obtained in terms of phosphorus.
Iron salt plus phosphoric acid.	0.25	85° C.	27° C.	52° C.	0.442	0.484	0.042
No. 27.	0.10	"	"	"	0.110	0.119	0.009
" 789.	0.10	"	"	"	0.021	0.022	0.001
" 344.	0.10	"	"	"	0.066	0.067	0.001
" 65.	0.10	"	"	"	0.012	0.012	0.000

As the arsenic in these determinations was precipitated under identically the same conditions as were previously used in our blank experiments, except phosphorus being present, it is reasonable to infer that the action is a mechanical one, the ammonium phosphomolybdate carrying down with it a little of the arsenomolybdate, the amount depending largely upon the size of the precipitate. Our results given above tend to demonstrate this quite conclusively. We repeated the above work using Wood's formula for molybdic acid, shaking for ten minutes instead of five, allowing the precipitate to stand for fifteen minutes before filtering off, to ascertain if any of these variations had any influence on the precipitation of arsenic. We found that they made no appreciable difference in our results. If the method is followed as outlined, and the temperature of the solutions is not higher than that specified, so that the actual temperature at which the shaking takes place does not exceed 49° to 55° C., the error will never be appreciable, except in the case of a steel very high in both phosphorus and arsenic. One point, however, we have been unable to check up, and that is if arsenic which has been reduced from the ore with the iron behaves the same as

arsenic artificially introduced. We were wholly unable to obtain a sample of steel containing an appreciable amount of arsenic, upon which to work, and have been obliged to leave this until some future time when we may be fortunate enough to secure the necessary sample.<sup>1</sup> It is conceded by every one that temperature is an all-important factor in the precipitation of phosphorus in the presence of arsenic. We know that above a certain temperature arsenic is sure to come down in greater or less amounts. The question then arises, how high a temperature is necessary for the complete precipitation of phosphorus, or in other words, how low a temperature can we use and feel sure we have precipitated all the phosphorus. Numerous experiments upon various samples of steel at 32° and 55° temperature have shown that the results at 32° C. are slightly lower. This difference does not usually exceed 0.001 per cent. if precautions are taken to thoroughly shake the solution, and to use a paper sufficiently close to hold every trace of the fine precipitate. In view of the fact that the difference between the results obtained at the two different temperatures is so slight, and also that there is danger of contamination in the case of a steel high in both phosphorus and arsenic, we adopted the lower temperature.

It may be asked how do the results obtained by this volumetric method compare with those given by gravimetric methods of wide reputation, such as the acetate method. We regret that we were unable to make acetate determinations of the phosphorus in the four standard samples of steel previously used, but our investigations of the molybdate method proved so much more exhaustive than we had anticipated, that these samples were used up in that work. However, we spent considerable time on a steel which had been examined by a number of well-known chemists. The results obtained by others are as follows:

Acetate method.				Molybdate method.			
0.047 per cent. phosphorus.				0.059 per cent. phosphorus.			
0.048	"	"	"	0.050	"	"	"
0.046	"	"	"	0.060	"	"	"
0.050	"	"	"	.....			

<sup>1</sup> Since writing the above we have received, through the kindness of Mr. W. P. Barba, of the Midvale Steel Company, a sample of steel said to contain 0.093 per cent. phosphorus, and approximately 0.12 per cent. arsenic. The average of a number of determinations on this sample, by the above method, gave 0.095 per cent. phosphorus—thus confirming what we had previously observed.



Our results on this sample were 0.048 by the acetate method and 0.055 by the volumetric. By the combination method described above, which seems to exclude many of the chances of error which occur in either the acetate or molybdate method, we found 0.0538 per cent. phosphorus.

It will be noticed that the results obtained by the acetate method are lower than either of the others. This has been our experience repeatedly, when we have compared the three methods, the acetate giving invariably the lowest results.

We will not enter into a discussion in regard to the causes for this as they are many, and this is not the purpose of our paper, but in our opinion the proposed Committee on Standard Methods can do no greater benefit to the iron industry of our country than by a thorough investigation of the methods used for the determination of phosphorus in ores and finished products. From our personal observation we know that frequently injustice is done, and able chemists brought into disrepute, simply because their results have not agreed with those obtained by analytical chemists of wide reputation, whose methods have not told the whole truth.

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### ON THE QUALITATIVE DETERMINATION OF TANNING MATERIALS.<sup>1</sup>

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IT can hardly be said that any systematic attempt has been made to formulate a scheme for distinguishing the various tanning materials by their qualitative reactions, except perhaps a very slight table published by the writer, although, in view of the constantly increasing number of new tanning materials, and especially of new extracts which are offered to tanners, the matter has become one of considerable practical importance. The commercial value of an extract is dependent, not only on the percentage of tanning matter as determined by analysis, but on the nature of the tannin present, which influences the character of the leather produced.

It is, of course obvious, that, failing a clear knowledge of the

<sup>1</sup> Read before the World's Congress of Chemists, August 25, 1893. Proof of this article was kindly read by Professor Henry Trimble.

tannins themselves any definite scheme of separation is for the present impossible; since, although we have good reason to believe that the tannins are a class, we are quite ignorant of their number, which may easily be a comparatively small one, as many members of the group which at present receive individual names are probably mere mixtures. What can be done is to separate the tanning materials into groups or individuals by reactions which have been empirically determined; of which in many cases we do not know the chemical significance, and which may possibly be often due to other constituents of the materials than the tannins themselves. The question is still further complicated by the fact that woods, barks, and fruit of the same tree often yield tannins of distinctly different character. In view of these facts, the group tables given must be only regarded as pointing out the general character of the material examined, and their indications must always be confirmed by direct comparison of *all* the reactions observed with those given by the material suspected. It must also be remembered that in some cases the group reactions are uncertain, or may be simulated by mixtures, which may often be determined by comparison of the results of the more special tests.

In this connection it may be noted that most of the reactions under the intermediate groups might be simulated by suitable mixtures of A and F; and that the inconstancy of the iron reaction in closely allied trees, points either to their containing mixtures of tannins, or to the existence of a very large number of closely allied tannins of very similar constitution. The point is one very difficult of decision, since we have no really reliable method for separating different members of the family.

It was thought that some information as to the meaning of the reactions employed might be obtained by examining the behavior of the simpler derivatives under the same circumstances, and the results are given in table X. It will be at once obvious that the blue-black reaction with iron is characteristic of the pyrogallol group; and the green-black equally so of the catechol derivatives, while phloroglucol, contrary to the statements of the text-books, gives no marked reaction with iron, but is alone characterized by the very delicate reaction

with the vanillin present in deal. On the remaining reactions little light is thrown.

In qualitative work with tanning materials, a good deal depends on the strength of the solutions, and the way in which the tests are performed, and as the information in the Tables is necessarily very brief, a few preliminary words are desirable.

*Infusions of tanning materials* are understood to be of about the strength used by the writer in determinations by hide-powder, *viz.*, about 0.6 gram of dry soluble matter in 100 cc., but moderate divergencies from this do not influence results. Of course where reactions are feeble in any case, with very dilute solutions they may be imperceptible, and on the other hand, strong solutions will sometimes give precipitates where only colorations are noted with weak ones.

*Bromine water reaction.*—It is best to add the bromine water drop by drop to 2–3 cc. of the infusion in a test tube, until the solution smells strongly. In some cases the precipitate is slight, or forms slowly, and occasionally it is crystalline and on this account less conspicuous, but it is usually a distinct yellow or brown flocculent one. In most cases bromine precipitates such tannins as give a green-black with iron, and in general terms it may be said to be a reagent for the catechol tannins.

*Nitrous acid reaction.*—This reaction, which is believed to be a new one, is obtained by adding to a few cc. of the infusion in a porcelain basin a distinct excess of solution of sodium or potassium nitrite, and then 3–5 drops of decinormal sulphuric or hydrochloric acid. In typical cases the solution instantly turns pink or crimson, and slowly changes through purple to a deep indigo-blue, but in others, as sumach where the reaction is feeble, and masked by other changes, the final color is green or even brownish. In a large number of cases, nitrous acid produces a yellow or brown coloration or precipitate, but “reaction” in the Tables invariably means a series of color-changes as above described. Nothing can as yet be said on the nature of the chemical changes produced. The reaction is given by all tanning materials which yield ellagic acid or “bloom,” but not by ellagic acid itself, nor by pure gallotannic acid. It is possibly a reaction of ellagitannic acid.

*Ferric alum, Ammonio-ferric sulphate.*—A one per cent. solution of this salt has been chosen as easily obtainable, neutral, and in a state of approximate purity. Ferric chloride, which is generally used, is almost invariably strongly acid, and of a very persistent yellow. Acid ferric chloride in excess will give a green-black reaction with gallotannic acid itself, and its results as a test are often very misleading. Ferric acetate, which has also been largely used gives heavy precipitates with most materials and is very strongly colored, so that it was found less convenient than the iron alum. As the colorations are generally very powerful, they are best seen by diluting the tannin infusion freely, and adding the iron solution very cautiously. In many cases the coloration first produced, and which is the characteristic one, rapidly fades to a dull olive or brown in presence of excess of iron, probably by oxidation and destruction of the tannin.

*Cupric sulphate and ammonia.*—When solution of cupric sulphate is added to a tanning material infusion, it sometimes gives a precipitate, and sometimes not. This is a useful indication in some cases, but must not be regarded as of first rate importance as the presence of any weak organic salt would in all cases cause a precipitate, by neutralizing the sulphuric acid of the sulphate. Cupric acetate produces a precipitate with all tannins so far as I have observed, and it is interesting to note that in this case, as in many others of a like character, the tannin combines with, and precipitates the salt as a whole. On the addition of ammonium carbonate, effervescence takes place, and the precipitate darkens, and becomes a true tannate.

When ammonia is added to the mixture of a tannin and cupric sulphate, a precipitate is invariably formed in the first instance, consisting of a tannate of copper with variable quantities of blue cupric hydroxide. With excess of ammonia, the whole of this precipitate is in many cases dissolved, while in others, an insoluble tannate remains. The latter is the case with all tannins derived from gallotannic acid and with many containing protocatechuic acid and forms a useful means of classification, though as yet the difference of structure to which it corresponds is unknown. The fact that hemlock and other

pine barks, as well as cutch and gambier, yield cupric tannates soluble in ammonia is an instructive commentary on processes which have been proposed for quantitative estimation by precipitations by ammonio-cupric solutions.

Where the precipitate redissolves it generally does so with the production of either a greenish brown, or a purplish brown coloration, which in presence of a small amount of the blue ammonio-cupric sulphate, appears either as a green or a reddish violet, and is again a useful means of identification. It need hardly be pointed out that to see this coloration well, the copper should be in the least possible excess. Hence it is desirable to use a very weak copper solution, say at most one per cent.

*Stannous chloride and hydrochloric acid.*—This reagent, the application of which is here first published, consists in a strong solution of stannous chloride in concentrated hydrochloric acid. If about ten cc. of this are added to one cc. of the tanning material infusion, in a porcelain basin, and allowed to stand for ten minutes, coniferous tans, mimosas, and some others give a very marked pink coloration. This is specially distinct in the case of larch bark. If a small piece of larch-tanned leather be steeped in the reagent, the coloration appears very strongly.

*Deal shaving and Hydrochloric acid.*—A shaving or slip of any pine wood is moistened with the infusion, and then, either before or after drying, is again moistened with concentrated hydrochloric acid. In the case of cutch and gambier, and a few other materials, the spot becomes at once a bright red or violet, but in many cases the reaction is faint, and only appears after some hours. It probably always indicates the presence of phloroglucol.

*Sodium Sulphite*—This was mentioned in my previous manuscript on the subject, but the printer unfortunately substituted sodium sulphide, which does not answer in the laboratory.

In some cases these reactions will serve to determine the constituents of mixtures but in many cases this will continue impossible till further and more distinctive reactions are discovered.

They can of course be applied to the recognition of tannates. when excess is present in leather which can be dissolved out

with water; but the effect of dilute alkalies and other solvents on the reactions is worth further experiment.

A few drops of the solution are placed in contact with a crystal of sulphite on a tile or in a basin. With valonia, a bright purplish pink is rapidly developed, apparently by oxidation. Many other tanning materials produce red or pink colorations, but in no case so marked a reaction as valonia.

*Concentrated sulphuric acid.*—A test tube is rinsed out with the infusion, and drained so that only about a drop remains, and concentrated acid is cautiously poured into the sloping tube, so as to form a layer underneath the tannin solution. The ring of color at the junction of the two liquids is noted, and then they are mixed by shaking, and diluted with water. About half the materials give a deep purplish crimson, called simply "crimson" in the Tables, and in many cases this is decidedly pink on dilution, while in other cases it is obscured by brown products formed by the heat of mixture. A large number of other materials give browns or yellows only, which when intense appear red, but dilute to yellows or yellow-browns.

*Lime water* is a most useful reagent, being very varied in the color of the precipitates it produces, and the changes they undergo by oxidation. The reaction is best seen in a shallow porcelain basin.

QUALITATIVE CLASSIFICATION OF TANNING MATERIALS. TABLE I.

Bromine water produces a precipitate.				Bromine water produces no precipitate.			
Nitrous acid gives no reaction or merely darkens.		Nitrous acid causes a red coloration, becoming violet and blue or green.		Nitrous acid gives no reaction or merely darkens.		Nitrous acid produces a red coloration changing to violet and blue or green.	
Iron alum green-black.	Iron alum blue-black.	Iron alum green-black.	Iron alum blue-black.	Iron alum green-black.	Iron alum blue-black.	Iron alum green-black.	Iron alum blue-black.
Copper sulphate followed by ammonia in excess.	Group B. Table V.	Group C. Table VI.	Group D. Table VII.	Group E. No members of this group known but catechol and protocatechuic acid, which are not tannins. See Table X.	Group F. Table VIII.	Group G. No members of this group known.	Group H. Table IX.

TABLE II.

Group A a.	Ferric alum.	Bromine water.	Nitrous acid.	CuSO <sub>4</sub> + NH <sub>4</sub> OH	SnCl <sub>2</sub> + HCl.	Deal shaving and HCl.	Na <sub>2</sub> SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Lime water.
Cutch from <i>Ac. catechu wood</i> .	Green-black.	pp.	No react. darkens.	pp. redissolves generally red-violet c/n.	No react.	Deep violet-red.	Reddens somewhat.	Red-brown coloration.	Reddish pp. slowly formed.
"Thaun leaf" extract ( <i>a cutch substitute</i> ).	Olive-black pp.	pp.	No react. darkens.	pp. redissolves brownish coloration.	No react.	No react.	No react.	Crimson, pink on dilution.	No pp.
"Turwar" bark. ( <i>Cassia auriculata</i> .)	Green-black.	pp.	No react. darkens.	pp. redissolves red-violet.	No react.	Trace.	Pink coloration.	Crimson.	Reddish pp.
"Gambene" extract (a gambier substitute).	Green-black coloration.	pp.	No react. darkens.	pp. redissolves red-violet.	No react.	No react.	Slight pink coloration.	Crimson-pink diluted.	Reddish pp.
"Tengah" bark ( <i>Cerriops Candolleana</i> ).	Green-black coloration.	pp.	No react. darkens. pp.	pp. redissolves red-violet.	Pink coloration.	No react.	Pink coloration.	Crimson.	Bright red pp.
Bark ( <i>Acacia leucophloea</i> ).	Green-black coloration.	pp.	No react.	pp. redissolves red-violet.	Pink coloration.	Slow violet react.	Pink coloration.	Crimson-pink diluted.	Dull brown pp.



TABLE III.

Group A. $\beta$ .	Ferric alum.	Bromine water.	Nitrous acid.	$\text{CuSO}_4$ + $\text{NH}_4\text{OH}$ .	$\text{SnCl}_2$ + $\text{HCl}$ .	Deal shaving and $\text{HCl}$ .	$\text{Na}_2\text{SO}_3$ .	$\text{H}_2\text{SO}_4$ .	Lime water.
Gambier, (ext. of leaves of <i>Nauclea gambier</i> ).	Deep green colorations	pp.	No react. darkens.	pp. redissolves olive-green.	Yellow.	Deep violet-red.	Yellow.	Crimson dilutes brown.	No pp.
(1) "Purim Bast," (leaves of <i>Colpoon</i> or <i>Oxyris compressa</i> ).	Green-black.	pp.	No react.	No pp. redissolves green.	No react.	Pink.	Yellow.	Crimson dilutes brown.	Light yellow pp.
(2) "Koko" natal, (leaves of <i>Celastrus buxifolia</i> ).	Green-black.	pp.	No react.	No pp. redissolves green.	No react.	No react.	Yellow.	Dark brown.	Bright yellow pp.
Larch bark ( <i>Larix Europaea</i> ).	Green-black coloration.	pp.	No react. darkens.	pp. redissolves olive-green.	Pink coloration.	No react.	No react. darkens.	Deep red-brown.	Rusty pp.
Hemlock bark ( <i>Tsuga</i> or <i>Abies Canadensis</i> ).	Olive-green reddish pp.	pp.	No react. pink with $\text{NaNO}_2$ .	pp. redissolves neutral tint.	Pink coloration.	No react.	Reddens.	Crimson dilutes pinkish.	Red-brown pp.
"Larch" extract ( <i>Abies excelsa</i> ). (3)	Green-black or brown.	pp.	No react.	pp. redissolves olive-green coloration.	Pink coloration.	No react.	Darkens.	Deep red-brown.	Brown pp.

(1) Used at Cape of Good Hope as sumach.

(2) Used in Natal as sumach substitute.

(3) *Fichte*, *Kothlanne* Norway or common spruce. *Abies pectinata* the *Weiss* or *Eddel-Tanne* or silver fir is said to give a blue-black with iron

TABLE IV.

Group A γ.	Ferric alum.	Bromine water.	Nitrous acid.	CuSO <sub>4</sub> + NH <sub>4</sub> OH.	SnCl <sub>2</sub> + HCl.	Deal shaving and HCl.	Na <sub>2</sub> SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Lime water.
Willow bark. (Russian. Sp. unknown.)	Green-black.	pp.	No react.	Slight pp. — Dense pp.	No react.	Violet faint.	Pink coloration.	Red-brown not intense.	Slight greyish pp.
<i>Acacia Anglica</i> or <i>Populadencia macrocarpa</i> .	Green-black.	pp.	No react.	Slight pp. — Dense choice pp.	Pink or violet color.	Violet faint.	Reddens somewhat pink.	Crimson dilutes pink.	Reddish pp.
<i>Acacia catechu</i> bark.	Green-black.	pp.	No react.	No pp. — Dense violet-black pp.	Possible trace.	Trace.	Pink color.	Red-brown.	Flesh color pp.
"Thorn tree" bark. ( <i>Acacia horrida</i> ) (Cape.)	Green-black.	pp.	No react. darkens.	No pp. — Dense pp.	No react.	Doubtful.	Pink color.	Dull crimson not intense.	No pp.
Mangrove bark extract. ( <i>Rhizophora manglie</i> .)	Green-black.	pp.	No react.	No pp. — Reddish-black.	Slight reddening.	No react.	Slight reddening.	Red-brown.	Red pp. darkened by excess.
Quebracho wood extract. <i>Quebracho</i> or ( <i>Loxopterygium Lorentzii</i> .)	Green-black coloration.	pp.	No react.	Slight pp. — Dense pp.	Pink color pp.	Trace.	Doubtful.	Crimson coloration dilutes pink.	Light brown pp.
"Sugar brush" bark. (Cape.) ( <i>Protea mellifera</i> .)	Green-black.	pp.	No react. darkens.	No pp. — Dense pp.	No react.	Trace.	Doubtful.	Red.	Yellow-brown pp.
"Waagenboom" (Cape.) ( <i>Protea grandiflora</i> .)	Green-black.	pp.	No react. darkens.	No pp. — Dense pp.	No react.	Trace.	Pink color.	Crimson dilutes pink.	Light yellow pp.
"Kruppelboom" (Cape.) ( <i>Leucospermum conocarpum</i> .)	Green-black.	pp.	No react. darkens.	No pp. — Dense pp.	No react.	Violet distinct.	Pink color.	Crimson dilutes pink.	Slight greyish pp.
"Silver tree" (Cape.) ( <i>Leucodendron argentea</i> .)	Green-black.	pp.	No react. darkens.	No pp. — Dense pp.	No react.	No react.	Pink coloration.	Crimson dilutes pink.	Flesh color pp.

TABLE V.

Group B.	Ferric alum.	Bromine water.	Nitrous acid.	CuSO <sub>4</sub> + NH <sub>4</sub> OH.	SnCl <sub>2</sub> + HCl.	Deal shaving and HCl.	Na <sub>2</sub> SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Lime water.
"Skens" Cypress Sumach (possibly <i>Cornaria myrtifolia</i> ).	Blue-black pp.	pp.	No react.	Slight pp. Dark pp.	No react.	No react.	Yellow.	Yellow-brown.	Yellow pp. dark'ning
Kilphant bark (1) ( <i>Rhus Thunbergii</i> ).	Blue-black.	pp.	No react.	No pp. Dense dark pp.	No react.	No react.	Pink.	Dull crimson dilutes orange.	Pinkish pp.
Canalgre (Root of <i>Rumex hymenosepalus</i> ).	Blue-black pp.	pp.	No react.	Slight pp. Dense dark pp.	No react. clouds.	Trace violet.	Slight dark'ning	Yellow-brown.	Pink coloration greyish pp.
"Talwan" or "Glandshorties" (Root <i>Elaphantorrhiza Burchellii</i> ).	Blue-black pp.	pp.	No react. darkens.	Slight pp. Dense dark pp.	No react.	Trace violet.	Pink.	Red.	Reddish brown pp.
Mimosa or Wattle bark (Various Austral. Acacias).	Dirty violet pp.	pp.	No react.	Slight or no pp. Dense purple brown pp.	Slight reddening	Sometime's trace.	Reddens.	Crimson dilutes pink.	Reddish or yellow-brown pp.
Babool bark. India. ( <i>Acacia Arabica</i> ).	Dirty violet pp.	pp.	No react.	Slight or no pp. Dense dark pp.	Some trace.	Faint trace.	Slight dark'ning	Crimson dilutes orange.	Dark reddish brown pp.
Dark red Austr. bark (Probably an acacia).	Dirty violet pp.	pp. needle crystals.	No react.	Slight pp. Deep violet pp.	No react.	Faint trace.	Orange-pink.	Crimson dilutes pink.	Bright violet pp.
"White bark" <i>Algaroba blanca</i> South America ( <i>A. prosopis</i> or <i>acacia</i> ).	Dirty violet pp.	pp.	No react.	No pp. Reddish black pp.	No react.	Violet.	Reddens strongly.	Crimson dilutes pink.	Red pp. turning violet.

(1) Used at Cape of Good Hope.

TABLE VI.

Group C.	Ferric alum.	Bromine water.	Nitrous acid.	CuSO <sub>4</sub> and ammonia.	SaCl <sub>3</sub> + HCl.	Deal shaving and HCl.	Na <sub>2</sub> SO <sub>4</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Lime water.
Cork bark ( <i>Quercus suber</i> ).	Green-black coloration	pp.	Reacts somewhat.	Slight pp. — Brown color.	No react.	No react.	Reddens.	Crimson dilutes pink.	Reddish brown pp.
Green Oak (Ital.) ( <i>Quercus ilex</i> ).	Green-black coloration	pp.	Reacts faintly if at all.	Slight pp. — Brown color.	No react.	No react.	Reddens.	Crimson dilutes pink.	Reddish brown pp.
Garouille, Root Bark of Kermes Oak ( <i>Quercus Coccifera</i> ).	Green-black coloration	pp.	Reacts	Slight pp. — Brown color.	No react.	No react.	Reddens.	Crimson dilutes pink.	Reddish brown pp.
Quercitron Bark ( <i>Quercus Tinctoria</i> ).	Green-black coloration	pp.	Reacts somewhat.	Slight pp. — Brown color.	No react. Light green.	No react.	Doubtful.	Crimson dilutes pink.	Dyes yellow with Al. and Sn. mordants.
Chestnut Oak ( <i>Quercus Castanea</i> ).	Olive-green coloration	pp.	Reacts distinctly.	Decided pp. Insol. in excess.	No react.	No react.	Reddens.	Crimson dilutes pinkish.	Infusious fluoresces especially with ammonia.

TABLE VII.

Group D.	Ferric alum.	Bromine water.	Nitrous acid.	CuSO <sub>4</sub> and ammonia.	SaCl <sub>3</sub> + HCl.	Deal shaving and HCl.	Na <sub>2</sub> SO <sub>4</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Lime water.
English Oak ( <i>Quercus Robur</i> ).	Blue-black (green with excess).	pp.	Reacts somewhat.	Slight pp. — Dark brown pp.	No react.	Faint react.	Reddens.	Crimson dilutes pink.	Reddish brown pp.
Jaft or Delift. (1) Supposed oak product.	Blue-black pp.	pp.	Reacts red-blue.	Brown pp. — Dark brown pp.	No react. Dark brown pp.	Faint react.	Some dark'ning	Crimson dilutes pink.	Reddish brown pp.

(1) A Persian product, dark scales very rich in tannin (about forty per cent).

TABLE VIII.

Group F.	Ferric alum.	Bromine water.	Nitrous acid.	CuSO <sub>4</sub> , NH <sub>4</sub> OH	SaCl <sub>3</sub> , HCl	Deal shaving and HCl	Na <sub>2</sub> SO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	Lime water.
<i>Aleppo galla</i> (of <i>Quercus infectoria</i> ).	Blue-black pp.	No pp. slight scum.	Reacts red to blue.	G'nish pp. ——— Dark pp. insoluble.	Light yellow pp.	No react.	No react.	Greenish to dirty yellow.	Pale pp. turning bluish-green.
Sumach (leaf of <i>Rhus coriaria</i> ).	Blue-black pp.	No pp.	Reacts feebly.	G'nish pp. ——— Dk brown insol. pp.	No react.	No react.	No react.	Yellow.	Yellow pp. turning bright green.
Myrobalans ( <i>Terminalia chebula</i> ).	Blue-black pp.	No pp.	Reacts red to blue.	Yellow pp. ——— Dark insoluble pp.	No react.	No react.	Yellow.	Yellow.	Yellow pp. turning greenish.
Pomegranate rind ( <i>Punica granatum</i> ).	Blue-black pp.	No pp.	Reacts red to blue.	Brown pp. ——— Dk brown insol. pp.	No react.	No react.	No react.	Orange-brown.	Bright yellow pp. turning red with excess
Algarobilla (pod of <i>Cassiaipisia brevifolia</i> ).	Blue-black pp.	No pp.	Reacts red to blue.	S'ht g'n pp. ——— Dense dark pp.	No react.	No react.	Deep yellow.	Deep yellow-brown.	Bright yellow pp. darkens somewhat
Divi-divi (pod of <i>Cassiaipisia coriaria</i> ).	Blue-black pp.	No pp.	Reacts red to blue.	S'ht g'n pp. ——— Dense dark pp.	No react.	No react.	No react.	Crimson.	Yellow pp. turning red-purple.
Algarobo (probably pod of <i>Prosopis dulcis</i> ).	Blue-black pp.	No pp.	Reacts red to olive.	S'ht g'n pp. ——— Dense dark pp.	No react.	No react.	Yellow.	Yellow to olive.	Yellow pp. turning black.
Valonia (Cup of <i>Quercus Agilops</i> ).	Blue-black pp.	No pp.	Reacts red to blue.	No pp. ——— Dark reddish pp.	No react.	No react.	Purplish pink.	Deep yellow.	Yellow pp. turning red-purple.
"Oak wood" extract (oak or chestnut wood).	Blue-black pp.	No pp.	Reacts red to blue.	Pale pp. ——— Purple brown pp.	No react.	No react.	Reddens.	Yellow-brown.	Yellow pp. turning red-purple.

(1) Moderately strong potassium nitrite solution precipitates divi, but not *divi* oakwood solutions; pp. soluble in hot, or much cold water.(2) *Crude* chestnut wood extract may be distinguished from oakwood by its violet-reaction with ammonium sulphide (see "Gerber" No. 261, p. 157).

TABLE IX.

Group H.	Ferric alum.	Bromine water.	Nitrous acid.	CuSO <sub>4</sub> and ammonia.	SnCl <sub>2</sub> + HCl.	Deal shaving and HCl.	Na <sub>2</sub> SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Lime water.
Pure Galloannic Acid.	Blue-black pp.	No pp.	No react.	No pp. Dark pp.	No react.	No react.	No react.	Yellow.	Pale pp. turning blue.
Babool Pods. <i>Acacia Arabica</i> .	Blue-black.	No pp.	No react. darkens.	Slight pp. Dark green color.	No react.	Faint violet.	No react.	Reddish violet.	Pink color. No pp.

TABLE X.

	Ferric alum.	Bromine water.	Nitrous acid.	CuSO <sub>4</sub> and ammonia.	SnCl <sub>2</sub> + HCl.	Deal shaving and HCl.	Na <sub>2</sub> SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	Lime water.
Catechol.	Dark green coloration.	No pp.	Turns yellow.	No pp. Green color.	No react.	No react.	No react.	Green coloration.	No pp.
Protocatechuic acid	Dark green coloration.	No pp.	Turns brown.	No pp.	No react.	No react.	No react.	No react.	No pp.
Phloroglucol.	No react.	Bulky white pp.	Turns olive-green.	No pp. No pp.	No react.	Red-violet coloration.	No react.	Slight yellow.	No pp.
Pyrogallol.	Blue-black turning green and brown.	No pp.	Turns yellow.	No pp. Brown color.	No react.	No react.	No react.	Brown coloration.	Violet coloration rapidly turning brown.
Gallic acid.	Blue-black coloration.	No pp.	Turns brown.	No pp. Brown color.	No react.	No react.	No react.	No react.	White pp. rapidly turning blue.

## THE IMPORTANCE OF THE STUDY OF BIOCHEMISTRY.<sup>1</sup>

By E. A. DE SCHWEINITZ, WASHINGTON, D. C.

WHEN the controversy between the two schools of the vitalists and chemists as to the true cause of the diseases produced in animals by the inoculation of putrefactive organic matter was at its height, Panum, of Denmark, made some careful researches and extracted from putrid organic matter chemical substances, which, when perfectly free from every form of germ life, produced intoxication and death. But, he said the poison extracted from this putrid matter is undoubtedly a pure chemical compound, it may, however, be produced by a microbe, and both microbe and poison play their part in the disease.

Now more than fifty years later, though the microbial origin of most diseases has been thoroughly established, it has also been shown that the chemical products of these germs are the direct cause, in most instances, of the fatal effects. For example, in diphtheria the growth of the germ is but a local manifestation, while the poison it produces is distributed through the whole system. When, however, the germ has been discovered that is responsible for a disease or for other changes, to which we will presently refer, the door has but been opened for a study of the most interesting chemical problems that can be imagined. Germs in general are cells of protoplasm, and it is by a study of their actions and the changes which they produce that we can gain a better insight into the processes of life. Fortunately the majority of germs can be easily cultivated artificially, so that it is not difficult to obtain solutions of their products, but it is difficult to isolate these products from the solution and determine their nature. For the most part the substances produced by bacterial growth have been found to belong to two classes, the albuminoids and ptomaines, the latter corresponding closely in many of their properties and composition to the vegetable alkaloids. Our knowledge of the albuminoids, however, is very meager. We can divide them into certain general classes as 1, globulins; 2, albumoses (hemi-proteo or deutero albumoses); 3, alkali or acid albumen; 4, peptones, etc.; but with this we have only made a step in the dark as it has given no idea of the actual

<sup>1</sup> Read at the Baltimore meeting, December 28, 1893.

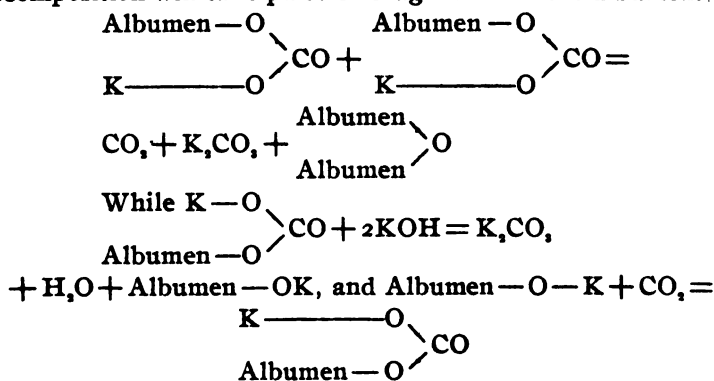
composition of the substances about which we speak, beyond that they contain carbon, hydrogen, oxygen, nitrogen, and sulphur, and phosphorus in certain proportions, and differ in coagulation. Do these apparent albuminoid substances from bacteria belong to the class of albumoses, or are they chemical diastases or ferments, many of the reactions of which they show? Can they be proved to be diastases by their hydrating and digesting action and shown to be allied to ptyalin, pepsin, etc.? At first it was held, and is still held by some, that the presence of albuminoid matter was necessary to the growth of the germ and that the products of the germ life were changes or simply decomposition products of the albuminoid matter upon which they fed. But it has been proven too that some of the same substances are obtained by the simple action of acids and alkalies upon albuminoids, and it is often difficult to decide whether the albumoses and alkaloids have been produced by the germs or by the alkali or acid. To decide this it is necessary to cultivate the germs upon solutions which do not contain a trace of albuminoid matter. This Fermi and Uschinsky have succeeded in doing with a number of different germs upon a solution of glycerine and mineral salts (ammonium phosphate, and acid potassium phosphate), and I have also with the hog cholera, glanders, and recently tubercle bacillus by the addition of asparagine to the above liquid. From these cultures albuminoid substances have been obtained as well as alkaloids, showing that they have truly been built up and elaborated by the germ and are to be compared to intercellular secretions and excretions of these minute forms of life, and not to simple products of decomposition from albuminoid matter in solution. That the products formed under the different conditions are similar is shown by the same physiological action of mallein prepared from these artificial cultures or from cultures upon beef broth. This power of the germ to multiply upon a solution of mineral salts where the carbon, hydrogen, nitrogen, and phosphorus are present in an easily assimilable form is not surprising, for we deal here with the lowest form of vegetable life, and it is well known that plants cannot live upon albuminoid matter directly, but only when by decomposition it has been reduced to its elementary condition.



The study of these products of the germ life has made but little progress so far as their actual chemical constitution is concerned. Much more attention has been paid to their physiological effect. It has been learned that some of these products will render an animal insusceptible to the action of disease germs, but what the chemical change which can have taken place and caused this immunity may be, is one of the problems for the biochemist and physiologist to decide.

It has been found too that the blood serum of animals that have been made immune to disease has a germicidal action and will render other animals immune. Where does this property lie? What chemical change again has the blood undergone?

In his studies upon the albuminoids of the egg, Scholl has indicated where this property may be. He found that egg albumen exerted a germicidal effect, that this germicidal power was destroyed by heat and could be restored by treating the albumen with alkali. This was similar to some of Buchner's observations upon blood serum, where he found the bactericidal property could be restored by the use of an alkali. Scholl's theory for explaining this, and also at the same time the coagulation of albumen, is that the normal albumen has a composition corresponding to a bicarbonate, that upon heating, carbon dioxide is given off and the albumen coagulated by the consolidation of two molecules, while when the alkali albumen is heated no decomposition will take place or coagulation of the albumen.



The carbon dioxide in the albumen is also set free by acid in the

cold which will explain the coagulation of albumen by acid. In the albumen molecule then, there is a group of atoms with a bactericidal action, which grouping is destroyed by heat and restored by alkali, just as there are certain groupings necessary for the production of a disinfectant, or rather just as the disinfectants are characterized by certain groups. The confirmation of these experiments will open up a field of enormous possibilities, as sulphur is an element which in many cases can replace oxygen, and the resulting compounds would be very interesting, as well as lead to a number of new products and eventually to a better understanding of the albuminoid molecule.

As just mentioned, it has been found that in the case of a great many diseases, animals can be made insusceptible by vaccination, and that the blood of such immune animals will make others immune. But this immunity only holds for the particular disease against which the animal was first vaccinated, and does not protect the animal against another disease. A guinea pig can be protected from a hog cholera inoculation by an injection of the albuminoid product extracted from the cultures. The same pig will die if inoculated with swine plague. If, however, it be vaccinated both for hog cholera and swine plague, with the products extracted from their respective cultures, the animal will be insusceptible to both diseases. Just in the same way in each particular disease some chemical change is produced in the blood or tissues and the work of the chemist should be to find out what these changes are. The possibilities are enormous, the difficulties many, but by careful study, accompanied necessarily with a certain amount of bacteriological work and the observation of pathological changes, we can hope to arrive at a more definite understanding of the process of life.

It is, however, not only with reference to diseases that a study of biochemistry is important. From a practical and commercial standpoint the work is useful. J. A. Davalos, of Havana,<sup>1</sup> describes the isolation of a distinct ferment and a number of bacilli from different tobacco leaves, some of which in artificial culture give distinct poisons. The different varieties of tobacco show different germs. These germs, by their growth upon the

<sup>1</sup> *Cronico Medico-gquirurgica de la Habana*, 1892. No. 15.

tobacco, give to it its peculiar flavor and odor, and the different qualities of tobacco owe their value to some particular ferment. As I have noticed, a bright yellow American high grade tobacco shows the presence of a germ altogether different, producing different substances from that of a low grade tobacco. Therefore, if the germs of a low grade tobacco can be destroyed and those from a fine tobacco substituted, we should be able to greatly improve the manufactured article. Now in practice, before the fermentation, some good tobacco is often mixed with the poorer grades to improve the quality. The manufacturer has learned by experience to make use of the different germs of the tobacco. But the chemist should not stop here. He should find out what the products of the growth of these germs are. This is possible because the germs can be isolated, cultivated, and the product of each individual germ determined, and eventually its identification or synthetic preparation.

Again, in Denmark, the practical manufacture of butter and cheese has been greatly advanced by the use of butter ferments, as they have been called. The flavor and aroma of butter and cheese are due to the products of a particular bacterium, or of several. Now these can and have been isolated, and to produce the best butter and cheese only those bacteria are used upon sterilized milk which give a desirable flavor, while normally those with undesirable products would also be present and interfere with the character of the butter and cheese. Here again the products of the growth of these bacteria should be studied, which in many instances would no doubt be found to be substances of easy synthetic preparation. It would be very much better to be able to add to a butter or cheese some particular extract which will impart the special flavor, rather than to have to inoculate the cheese and milk with a particular bacterium or mixture of bacteria for a desired quality. As has been well stated, we may see the time when each dairy is provided with a bacteria farm, and each particular brand of butter and cheese will have its corresponding originator, labeled and reared with as much care as is given to the cow from which the milk is obtained.

In their relation to the soil and plant life the germs and their

products are invaluable. Warrington and Winogradsky, in their isolation of the nitrifying organisms which convert nitrogenous matter into nitrites and nitrates, have thrown great light on the absorption of nitrogen by plants. Recently Winogradsky has described an organism which converts the nitrogen of the air directly into nitrates. Again, there are a number of germs that are ordinarily found in water or the soil which will reduce nitrates to nitrites or ammonia, as well as some pathogenic germs usually present in the soil which will flourish in artificial media in an atmosphere of nitrogen. We know that a subsoil, freshly turned, will not be productive until it has been exposed for some length of time to the air and moisture and to the action of the germs of the air. The plant does not take up directly in the form in which it exists in the soils, the mineral matter that it needs for its growth, but only when that is modified to a simpler form can it be utilized. Phosphorus is one of the elements which, whether combined in albuminoids or mineral salts, seems to be necessary for the growth of the germ, and is also necessary for the life of plants. By closely following the gradual changes in the artificial cultures of germs, we can arrive at a more definite understanding of the assimilation of mineral matter by the plant, as well as the fixation of carbon, the formation of starch and sugar, and possibly also, as has been suggested, of the building up of alkaloids.

I have only mentioned a few of the many directions in which a conjoint study of bacteria and their products are important with the desire of emphasizing the interest attaching to such investigations. It is along this line of research that the solution of many of the problems of life that have been a puzzle to both physiologist and chemist undoubtedly lies.

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### DETERMINATION OF THE CRYSTALLIZABLE SUGAR IN THE BEET.<sup>1</sup>

BY H. PELLET.

TRANSLATED AND ABSTRACTED BY G. L. SPENCER, WASHINGTON, D. C.

THIS is an extensive article including a résumé of practically all that has been written by the leading authorities upon

<sup>1</sup> Read before the World's Congress of Chemists, August 22, 1893.

the subject, in addition to original methods by the author. The paper is divided into five parts.

The first part contains a brief outline of the methods employed for the determination of sugar since the beginning of the industry, or in fact since the work of Margraff on the beet in 1747, and includes the literature of 1886.

In the second part is included a review of the principal prizes which have been awarded for researches on the estimation of sugar in the beet.

In the third part is given a résumé of the different methods which may be applied for the direct determination of the sugar, and the principal details of the new cold and warm aqueous methods, as applied in the manufacture of sugar and the analysis of mother beets.

In the fourth part is given an examination of the matters existing in the beet which influence the determination of the sugar, notably raffinose, pectic substances and asparagine.

Finally, in the fifth part, note is made of the purchase and sale of beets according to their quality, and an examination of the various methods employed for this purpose is included.

This abstract relates simply to that portion of the third part of the paper which includes methods original with the author.

PROCESSES WHICH MAY BE APPLIED TO THE ANALYSIS OF THE  
BEET FOR THE DIRECT DETERMINATION OF THE CRYSTALLIZABLE SUGAR WHICH IT CONTAINS.

The different methods may be divided into two classes, namely, chemical and physical (polariscopic). As the polariscopic methods are those usually employed we will omit a description of the chemical. The polariscopic methods may be divided into two groups; those employing alcohol as a solvent for extracting the sugar and those employing water. The process employing water, with which we shall specially deal, is that devised by the author and known as the method of instantaneous aqueous diffusion in the cold. In the instantaneous method, it is essential to obtain the beet pulp in an extremely fine state of division. Ordinary rasps cannot be employed for this purpose. For the analysis by this method the following rasps are recommended: First, for the analysis of entire beets, the conical rasps of Pellet

and Lomont as arranged by Keil; second, for the analysis of fragments of beets such as fresh cuttings for the diffusion process, the apparatus of R. Kiehle, of Leipzig; third, for the analysis of seed beets, or mother beets, in seed selection, the apparatus of Keil and Dolle, known as the *foret-râpe*. The rasp used in connection with the apparatus of Hanriot is applicable.

As has been stated, for this process the pulp must be in a very fine state of division, not merely forming a cream, but the particles must be regularly even. A suitable amount of the pulp, proper precautions being taken to protect it, is weighed into a flask of a definite volume. If the normal weight for the German instruments, 26.048 grams, is used the volume should be 201.35 cc., or if 25.87 grams of pulp be taken the volume should be 200 cc. The pulp is passed into the special flask with the assistance of a jet of water, then five to seven cc. of subacetate of lead (30° B.) are added and a little ether to reduce the foam, the flask being agitated with a rapid circular motion at the same time. The volume is now completed to 200 or 201.35 cc. as the case may be, and the contents of the flask thoroughly mixed. Filter and polarize after having acidulated the liquid with one or two drops of glacial acetic acid. A 400 mm. tube is used for the observation and gives the reading directly, corrected for the increase in volume of the solution. The diffusion is instantaneous and complete, permitting the filtration to be made as soon as the flask has been filled to the graduation and the contents thoroughly mixed. It is never necessary to heat the solution in order to insure complete diffusion, unless the water should be extremely cold, approximating 0° C. For all ordinary laboratory temperatures, the water will be sufficiently warm.

In order to make a large number of analyses per day, by this process, a filtration rack having six, twelve, or twenty-four holes, should be employed, also a continuous polariscope tube which will be described later on. Twelve to twenty flasks should be taken at once to the polariscope.

Among the different possible sources of error in the estimation of the sugar in the beet, those belonging only to the aqueous method will be here considered. In the aqueous process there is, of course, a possibility of the digestion or diffusion being incom-

plete, but this is very rare, since, owing to the simplicity of the operation, the flasks will always stand a sufficient time to obtain complete diffusion. In using the apparatus in the cold there is no danger at all of error, since a preliminary trial should be made to ascertain whether the pulp is sufficiently fine, and whether the water is of the proper temperature. There is a possibility of the solution of pectic substances which rotate the plane of polarization to the right. This error can only result from an insufficient amount of sub-acetate of lead. This inconvenience is easily avoided. The presence of pectic bodies may be shown in the following manner: Extract the pulp with cold water in large excess or with alcohol; treat the residue with boiling water and concentrate the liquid. This liquid will give a decided right-handed polarization amounting to more than 6.87 per cent. sugar on the weight of the beet. The same liquid, treated by sub-acetate of lead in sufficient quantity, will always polarize zero. Our work in this case is confirmed by Messrs. Chevron, Droixhe, and Weisberg.

Alcohol acts as sub-acetate of lead upon pectic matters and precipitates them entirely. It is for this reason that in the alcoholic solution two or three drops of sub-acetate of lead are sufficient for clarification, and for the complete precipitation of the pectic matters. It is hence easy to see how different results may be obtained in using the alcoholic or the water method upon the same pulp. Such differences might amount to from two to three per cent. of sugar calculated on the weight of the beet. As we have become better acquainted with the sources of error, the experiments have been repeated, and the adversaries of the aqueous method have all recognized that there are no plus polarizing substances in the beet not precipitable by lead and which are only thrown down completely, as they have stated, by alcohol.

In 1886 and 1887 many chemists published articles in which they attempted to demonstrate that alcohol, in fact, furnished results lower than those obtained by the water method, and which they then attributed to some particular substances precipitable by alcohol, and not by the sub-acetate of lead. But all have acknowledged later on that there were evidently diverse causes of error in their experiments, and have published statements

reviewing those made in their first papers, and have shown perfect concordance between the alcoholic and aqueous methods, when properly carried out. This is quite valuable, since at first the aqueous methods were vigorously attacked by critics who now acknowledge their reliability. There is still another possible source of error in the aqueous method in the cold. This is caused by air bubbles remaining attached to the pulp, and may be due to an insufficient use of ether, to ether being replaced by alcohol, to insufficient agitation, or to other faulty manipulations. This error, it may be seen, is easily obviated. Numerous parallel experiments have demonstrated that the aqueous instantaneous method in the cold, gives practically the same results as those obtained by either the alcoholic or the hot water methods.

APPLICATION OF THE INSTANTANEOUS AQUEOUS DIFFUSION  
PROCESS IN THE COLD TO THE EXAMINATION  
OF MOTHER BEETS.

A portion of the pulp may be removed from the beet by the *foret-râpe* of Keil and Dolle and analyzed as described. This requires simply a weighing and the usual manipulation. A simpler method, and one which will be described more in detail, obviates all weighings. In this method of working, that is without weighing, 8,300 analyses per day have been made in the establishment of Mr. Legras, and in the sugar house of Vaux sous Laon.

In the analysis of beet mothers without the use of a balance, the sound invented by Lindeboom is employed. This sound is so arranged that by the movement of a lever, a knife is made to penetrate the beet and remove a portion of it. A proper arrangement is provided for inclining the beet at a proper angle to the knife. The knife is arranged with parallel blades which are adjustable, and which will remove a cylindrical portion of the beet of a size which is perfectly under the control of the operator. After adjusting the knife to cut a cylinder of a certain size, which is determined by the convenience of the operator, it may be used for a number of samples and will cut a cylinder of practically the same weight at all times. The weights of the following cylinders cut in this way will give an idea of the accuracy of this method:



No.	Weight, grams.
1.....	6.245
2.....	6.265
3.....	6.290
4.....	6.370
5.....	6.245
6.....	6.285
7.....	6.365
8.....	6.250
9.....	6.335
10.....	6.240
11.....	6.330
12.....	6.390
13.....	6.370
14.....	6.270
15.....	6.310
16.....	6.300

Average, 6.304 grams.

If one will consider a beet of average richness as containing fifteen per cent. sucrose the minimum weight given in the above list would show 14.85 sugar and the maximum 15.2, an extreme difference of 0.35 or 0.15 to 0.20 above and below the mean. These figures approximate the required weight with sufficient accuracy for actual practice and for use with the special apparatus devised by Hanriot, we have found it a very valuable adjunct. Hanriot's apparatus is so arranged that the sample of beet, of the required weight, when placed in a proper receptacle is transferred to a mill where it is ground to a fine pulp. Immediately after grinding, by a suitable manipulation of a valve and rubber bulb containing water, the fine pulp is washed into the sugar flask and is ready for analysis. The Hanriot apparatus is then quickly washed, by means of a special valve arrangement, and is ready for another sample. Preliminary to commencing the analytical work, the sound is adjusted to give the most convenient weight of pulp, for the polariscope in use. This may be 6 grams, 5.12 grams, or 4.05 grams, according to the requirements of the instrument. But little adjustment is necessary to so set the knives that they will cut a cylinder of the proper diameter and length to give the required weight. In this class of analysis, it is unnecessary to take account of the influence of the volume of the marc of the beet.

In the analysis of seed beets, Mr. Hanriot has suggested the use of electric signals for assorting the roots. Electric contacts are arranged on the scale of the instrument so that when this is turned to a certain point, corresponding to a certain richness of the beet, a signal will be sounded on a bell, and when turned to a certain other point a signal will be sounded on a bell of different tone, indicating in general the richness of the sample and showing the workmen how to distribute the roots.

#### CONTINUOUS TUBE FOR THE POLARIZATION OF ALL SOLUTIONS.

In many cases the manufacturer of sugar, the refiner or the seed producer, is obliged to make a very large number of analyses of the same class and as rapidly as possible. The work required in seed selection is an example. In this industry it is often necessary to make 3,000, 4,000, 5,000, and even 8,000 or more analyses of mother beets in a day.

With ordinary apparatus it is admitted that with one polariscope a single observer may make from 500 to 600 or even 1,000 analyses in a day, provided one has a sufficient number of observation tubes, that is, from twenty to fifty. The continuous tube permits this work with much less labor, far greater rapidity and requires but one observation tube. This instrument was devised especially for use in the analysis of mother beets.

Many difficulties were overcome before this tube was constructed in a satisfactory form. As now used there is a small tube at each extremity, one of which is termed the funnel and connects directly and exactly at the extremity of the observation tube against the glass; the other is a similar tube but is placed at a slight angle with the observation tube. This small tube connects with the sink and is used to get rid of the solutions after they have been polarized. This arrangement of the observation tube permits the displacement of one solution by another. In practice, the observation tube is never removed from the polariscope. At the start it is filled with water, slightly acidulated with acetic acid, care being taken to remove all air bubbles. The solution to be observed is now passed in at the funnel tube displacing the water, driving it out through the tube at the opposite end. When another solution is ready for examination, it is

simply necessary to pour it into the funnel and, as before, displace the preceding solution. The chemist at the polariscope will at first observe striae, which diminish rapidly, and finally the solution will become perfectly clear. As soon as the liquid becomes clear the observation may be made. While the chemist is entering the reading in his note book, an assistant introduces a new solution at the funnel, and the instrument is ready for another observation. In this way an observer can easily make four readings in a minute, but even if he could make but two, he would attain a speed twice as great as is possible with the ordinary polariscopic methods and with far less labor. In the analysis of beet mothers, where a slight difference is of no importance, an observer can easily make from six to ten readings per minute.

A special disposition of the apparatus may be made which permits filling the tube by siphonage. In this way from eight to twelve solutions per minute may be polarized.

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### EXPERT TESTIMONY.

BY WM. P. MASON.

A NUMBER of years ago several very able articles appeared in *Nature*, upon the subject of Expert Testimony, showing how desirable it is to have the scientific witness removed as far as possible from the position of a partisan, and suggesting that such an end could be best obtained by having the experts employed by the bench rather than by the bar. Some recent experiences of my own, which I beg permission to recount, call to my mind those "Nature" articles very forcibly. A poison case in which I was lately employed, may be roughly outlined as follows:

Much arsenic and a very little zinc were found in the stomach.

The body had not been embalmed, but cloths wrung out in an embalming fluid containing zinc and arsenic had been spread upon the face and chest.

Medical testimony showed that no fluid could have run down

<sup>1</sup> Read at the Baltimore meeting, December 28, 1893.

the throat. Knowing the relative proportions of zinc and arsenic in the embalming fluid, the quantity of arsenic found in the stomach was twelve times larger than it should have been to have balanced the zinc also there present, assuming them to have both come from the introduction of the said embalming fluid by cadaveric imbibition. Other circumstantial evidence was greatly against the prisoner.

At the time of my appearing for the people, on the occasion of the first trial of the case, my direct testimony brought out very strongly the fact of a fatal quantity of arsenic having been found in the stomach, but no opportunity was given me to testify to the presence of the zinc found there as well, although the fact of its existence in the body was known to the prosecution through my preliminary report. Through ignorance of the nature of such report on the part of the defence, no change was made in the character of my testimony during the cross-examination, and I was permitted to leave the witness-stand with a portion of my story untold. No witnesses were called for the defence, and the case was given to the jury with the darkest of prospects for the prisoner.

For many reasons, unnecessary to recount here, I was distinctly of the opinion that murder had been committed, but I felt nevertheless that common justice demanded that the prisoner should have been entitled to whatever doubt could have been thrown upon the minds of the jury, no matter how far-fetched the foundations for such doubt might have been.

The first trial having resulted in a disagreement of the jury I was pleased to learn, before the second hearing of the case began, that the defence was prepared to go into the question of the embalming fluid, for the responsibility of permitting only a part of what I knew to be drawn from me, to the entire exclusion of the remaining portion, was greater than I wished to assume. The nature of my report to the coroner having been established, and certain opinions relating thereto having been fully ventilated, the jury were possessed of "reasonable doubt" and acquitted the prisoner. What now were the duties of the expert upon the occasion of the first trial of this case and how should he have constructed the meaning of his oath.

One eminent legal light, to whom the question was referred, held that the expert was distinctly the property of the side employing him, and that his duty was simply to answer truthfully the questions put to him, without attempting to enlighten the court upon facts known to him, but not brought out by the examination, no matter how vital such facts might be.

Another held that although the above course would be proper in a civil case, yet in a matter involving life and death the witness should insist upon the court becoming acquainted with his whole story. Do not such differences in legal opinion make it yet more desirable that the expert, at least in capital cases, should be the employee of the bench, rather than of the bar, in order that whatever investigations are made may be entirely open to public knowledge and criticism?

DISCUSSION.—Dr. Wiley: I hope that at some time in the future we shall be able to discuss this subject more fully. It is one which vitally interests most of us.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 2.]

## A NEW METHOD OF ANALYZING FATS AND RESINS.

By PARKER C. McILHINEY, Ph.B., A. M.

Received January 5, 1894.

A number of processes have been proposed and used for the analysis of fats depending upon the power possessed by their unsaturated constituents to absorb by direct addition two or four atoms of bromine or iodine.

Allen, *Analyst*, **6**, 177, proposed the use of an aqueous solution of sodium hypobromite to be added to a weighed quantity of the oil together with sufficient hydrochloric acid to liberate the bromine which then acts upon the oil. An excess having been added its amount is determined with sodium thiosulphate after adding potassium iodide.

Mills and Snodgrass, *J. Soc. Chem. Ind.*, **2**, 436 added a solution of bromine in carbon disulphide to a solution of the fat in the same solvent until an excess has been added as indicated by the red color of the bromine remaining permanent for fifteen

minutes, and then a solution of potassium iodide and determined the excess with thiosulphate.

Mills and Akitt, *J. Soc. Chem. Ind.*, **3**, 65, proposed to substitute carbon tetrachloride for carbon disulphide and to determine the excess by a solution of  $\beta$  naphthol in the same solvent.

Hübl, *Dingler's Poly. J.*, **253**, 281, and *J. Soc. Chem. Ind.*, **3**, 641, suggested the use of a solution containing twenty-five grams of iodine and thirty grams of mercuric chloride dissolved in one liter of alcohol, a known measure of the reagent to be added to a weighed portion of the oil and allowed to remain tightly stoppered for a certain length of time when the excess is determined with thiosulphate.

Levallois, *J. pharm. chim.*, 1887, **1**, 334, used bromine water, adding it, in just sufficient excess to slightly color the liquid, to the fatty acids obtained from the oil suspended in water.

Halphen, *J. pharm. chim.*, 1889, **20**, 247, used bromine water in excess determining the amount of excess with sodium hydroxide.

Gantter, *Ztschr. anal. chem.*, 1893, 178, suggested the use as a reagent of iodine dissolved in carbon tetrachloride.

The aim of all these processes is to determine the amount of halogen which the substance under examination will absorb by addition, but the figures obtained represent this only approximately even when substances which easily form substitution products are absent. Some substitution takes place with almost all oils, and with rosin oil, rosin, and probably most other resins, substitution causes the entire absorption.

The extent to which this substitution takes place depends upon the nature of the substance operated upon, and varies with different oils and resins, and a determination of the amount of halogen so absorbed may serve as a means of identifying and in some cases determining them.

The following process has been devised for determining the amount of bromine which oils and resins can absorb by addition, (which will be called the "Bromine Addition Figure"), and at the same time the amount of bromine which replaces hydrogen the action being allowed to continue eighteen hours in the dark; this gives the "Bromine Substitution Figure." The first figure

gives in most cases the same information as the Hübl figure but is more reliable, while the second figure is a measure of the activity of the saturated constituents toward bromine.

It depends upon the fact that bromine in forming substitution compounds forms a molecule of hydrobromic acid for every atom of bromine which replaces hydrogen, while in forming additive compounds no hydrobromic acid is formed.

It was found impossible to use iodine alone as the addition figures are then very much too low and there is little difference between the substitution figures of bodies of unlike character.

The following solutions are used :

Bromine in carbon tetrachloride.....	$\frac{N}{8}$
Sodium thiosulphate.....	$\frac{N}{10}$
Potassium hydroxide.....	$\frac{N}{10}$

0.250-1.000 gram of the substance is dissolved in ten cc. of carbon tetrachloride in a bottle of 500 cc. capacity provided with a carefully ground glass stopper. An excess of bromine solution is added, the bottle tightly stoppered and placed in a dark closet. No water or alcohol should be present and light should be excluded as far as practicable. At the end of eighteen hours the bottle is cooled with ice to form a partial vacuum, and a piece of wide rubber tubing about one and one-half inches long is slipped over the lip of the bottle so as to form a well about the stopper. This well is filled with water and the stopper carefully lifted when the water will be sucked into the bottle and dissolve the hydrobromic acid present. When about twenty-five cc. of water have been added in this way, the bottle is well shaken and 10-20 cc. of twenty per cent. potassium iodide solution added. The excess of bromine acts on the potassium iodide, liberating a corresponding amount of iodine which is titrated with  $\frac{N}{10}$  thiosulphate after adding about seventy-five cc. more water, using starch as an indicator. The total bromine absorption is calculated from the difference between the amount of thiosulphate required for the bromine solution added and the amount required for the excess. The contents of the bottle are now transferred to a separatory funnel and the aqueous portion separated, filtered through a cloth filter, a few drops of thiosulphate added if the solution is blue, and this is then titrated with  $\frac{N}{10}$  potassium

hydroxide using methyl orange as indicator. The end reaction is best observed by using a porcelain casserole to contain the solution, adding the alkali in slight excess and titrating back with  $\frac{N}{10}$  hydrochloric acid until the pink acid tint just reappears. From the number of cubic centimeters of alkali used the amount of bromine present as hydrobromic acid is calculated, and when expressed in per cent. gives the bromine substitution figure because for every atom of bromine which has replaced an atom of hydrogen, one molecule of hydrobromic acid has been formed. Twice the bromine substitution figure subtracted from the total absorption gives the bromine addition figure.

The following results were obtained :

Substance.	Total bromine absorption, eighteen hours.	Bromine, addition figure.	Bromine, substitution figure.
W. G. Rosin.....	212.7	0.0	106.35
E. Rosin.....	206.5	0.0	103.25
Second run Rosin Oil (a).....	116.2	0.0	58.1
"    "    "    "    (b).....	114.7	0.0	57.35
American Raw Linseed Oil ...	102.88	102.88	0.0
Same Oil Boiled.....	103.92	103.92	0.0
White Salad Cotton-seed Oil..	65.54	64.26	0.64
Sperm Oil .....	56.60	54.52	1.04

A consideration of the above figures shows that the results are much more instructive than those obtained by the Hübl process which is the one in common use. Rosin oil, rosin, and other resins may be detected and determined in mixture with fatty oils, or, if they are present in known quantity, the character of the fatty oil may be determined. Investigations which are being made on a large number of oils and resins will probably furnish analytical data for the analysis of oils and varnishes.

## ON THE DETERMINATION OF PHOSPHORIC ACID.<sup>1</sup>

BY H. PEMBERTON, JR.

LAST autumn I described a process for determining phosphoric acid by titration of the ammonium phosphomolybdate with standard alkali. (This JOURNAL, 15, 382.) The ratio

<sup>1</sup> Read at the stated meeting of the Chemical Section of the Franklin Institute, held February 20, 1894.



between the  $P_2O_5$  of the precipitate and the standard alkali was determined and found to be 23.2 molecules of  $Na_2O$  to one molecule of  $P_2O_5$ . Upon this ratio, as determined by direct analysis, the standard solution was prepared of such strength that one cubic centimeter should be equal to one milligram of  $P_2O_5$ , by diluting 326.5 cubic centimeters of normal alkali to one liter. The analyses upon which this ratio (23.2 molecules) was determined were carefully made. I was, therefore, at a loss to know the cause of the variation of this figure from the theoretical ratio of exactly twenty-three molecules of  $Na_2O$ . The difference is of more importance than might at first thought, be supposed, since the strength of the alkali solution is based upon the figure determined empirically, and not upon the theoretical one. If the 23.2 proportion is wrong and twenty-three correct, a standard solution based upon the former ratio would give too low results in the proportion of 23.2 : 23.0. Thus a phosphate rock containing eighty per cent. calcium phosphate would appear, by such an analysis, to contain only 79.31 per cent.

It was decided, therefore, to repeat this part of the work, and in this re-examination the conditions were the same as those previously existing, except in one particular: the amount of phosphoric acid operated upon was smaller than that previously used. By referring to the original paper, it will be found that about eighty cubic centimeters of alkali were used in each of the titrations in question. This represents a quantity of the yellow precipitate much larger than would ever be obtained in the analysis of even the richest phosphate rocks; and in operating upon so large a precipitate the liability of error from incomplete washing is great. Any free acid remaining in the precipitate would, of course, result in too high a reading of the burette, with a corresponding error in the standardizing of the solution.

The following are the results obtained in this re-examination:

Some di-sodium hydrogen phosphate, bought as chemically pure, was dissolved in hot distilled water, filtered, and crystallized; the crystals were washed, dissolved again in water, and recrystallized. Of the resulting crop of crystals, about forty-five grams were dissolved in one-half liter of water. The strength of this solution was then determined.

	Weight of $\text{Na}_2\text{HPO}_4$ solution, grams.	Grams.	
I.....	20.0814	gave 0.7581	$\text{Na}_4\text{P}_2\text{O}_7$
II.....	17.9585	gave 0.6778	$\text{Na}_4\text{P}_2\text{O}_7$
III.....	36.9115	gave 1.1652	$\text{Mg}_2\text{P}_2\text{O}_7$

The magnesium-ammonium phosphate precipitate was filtered, dissolved in acid and reprecipitated by ammonia.

By a coincidence each of these three determinations gave precisely the same result; *viz.*,

TABLE I.

	Grams $\text{P}_2\text{O}_5$ in 10 grams of solution.
I.....	= 0.2014
II.....	= 0.2014
III.....	= 0.2014

Therefore, ten grams of the sodium phosphate solution contained 0.2014 grams  $\text{P}_2\text{O}_5$ .

Weighed portions of this same solution were now precipitated by ammonium molybdate, thoroughly washed and titrated. The results are given in Table II.

TABLE II.

I.	II. Grams $\text{Na}_2\text{HPO}_4$ solution taken.	III. Equiva- lent to grams $\text{P}_2\text{O}_5$ .	IV. cc. of KHO solution used.
A.....	2.0410	0.04110	41.05
B.....	2.3710	0.04775	47.70
C.....	2.2920	0.04616	46.20
D.....	2.4690	0.04972	49.60

Dividing the figures in Column III by those in Column IV, and multiplying the result by 100, we obtain the number of milligrams corresponding to 100 cubic centimeters of the potassium hydroxide solution, as follows:

TABLE III.

	Mgms. $\text{P}_2\text{O}_5$ .
A.....	= 100.12
B.....	= 100.11
C.....	= 99.91
D.....	= 100.24
Average.....	= 100.09

Therefore, 100 cubic centimeters of the potassium hydroxide

solution neutralize an amount of the yellow precipitate corresponding to 100.09 milligrams of  $P_2O_5$ .

The standard acid was now titrated against the standard alkali, using phenolphthalein as the indicator, whereby the two solutions were found to be of exactly equal strength.

The standard acid was then titrated against pure sodium carbonate, using phenolphthalein at boiling heat:

	Grams $Na_2CO_3$ used.	cc. of acid used.	100 cc. acid equal to mgms. $Na_2CO_3$ .
I.....	0.9099	52.95	1719
II.....	0.9168	53.35	1719

Therefore, 100 cubic centimeters of acid are equivalent to 1719 milligrams sodium carbonate, and since the alkali solution is of the same strength as the acid, 100 cubic centimeters of it also are equivalent to 1719 milligrams sodium carbonate.

As we have already seen, by Table III, that 100 cubic centimeters of the alkali are required to neutralize 100.09 milligrams of  $P_2O_5$  (in the form of ammonium phosphomolybdate), it follows that 1719 milligrams sodium carbonate are required for 100.09 milligrams  $P_2O_5$ .

Dividing each by its molecular weight we have

$$\begin{aligned} \text{for } P_2O_5, \frac{100.09}{142.06} &= 0.7045 \\ \text{for } Na_2CO_3, \frac{1719.0}{106.1} &= 16.20 \end{aligned}$$

Therefore,

$$P_2O_5 : Na_2CO_3 = 0.7045 : 16.20 = 1 : 22.99$$

In other words, 23 molecules of sodium carbonate (or of  $Na_2O$ ) are required to neutralize the yellow precipitate containing one molecule of  $P_2O_5$ , and the former figure (that given in my paper of last autumn) 23.2 molecules, is incorrect.

Referring to Table II of the present paper, it may be stated that in analysis A the yellow precipitate was washed on an ordinary filter without using suction, the precipitate being washed on the filter, transferred to the beaker and then again filtered and washed. In analysis B, of the same table, the precipitate was washed on the ordinary filter, with the aid of the suction pump. In analyses C and D, the precipitates were washed with suction on a porcelain funnel with a fixed perforated plate in it.

This form of funnel is known as the Hirsch funnel.<sup>1</sup>

As in all cases the results were nearly identical; it is evident that the different methods of washing the precipitate had no influence upon the result. Exactly twenty-three molecules of  $\text{Na}_2\text{O}$  are required for one molecule of  $\text{P}_2\text{O}_5$ . The standard acid is prepared by diluting 323.7 cubic centimeters of normal sulphuric acid to one liter, and not 326.5 cubic centimeters as previously stated. The alkali solution, after removing carbon dioxide by barium hydroxide, is brought to the same strength as the acid, volume for volume.

One cubic centimeter of either solution is then equal to one milligram of  $\text{P}_2\text{O}_5$ .

PHILADELPHIA, PA., February 20, 1894.

### NOTE ON PEMBERTON'S METHOD OF PHOSPHORIC ACID DETERMINATION AS COMPARED WITH THE OFFICIAL METHODS.<sup>2</sup>

BY WM. C. DAY AND A. P. BRYANT.

HAVING occasion to make a series of determinations of phosphoric acid in Florida phosphate rock, we have used the method recently described by Mr. H. Pemberton, Jr., and incidentally have made a number of comparisons between it and the official method. The following are the results:

#### GRAVIMETRIC DETERMINATIONS.

- No. 1. From 0.7867 gram  $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$ , obtained 0.2426 gram  $\text{Mg}_2\text{P}_2\text{O}_7$
- No. 1. From 1.1100 grams  $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$ , obtained 0.3433 gram  $\text{Mg}_2\text{P}_2\text{O}_7$
- No. 2. From 1.0000 gram Florida rock, obtained 0.5828 gram  $\text{Mg}_2\text{P}_2\text{O}_7$
- No. 3. From 0.3807 gram Florida rock, obtained 0.0262 gram  $\text{Mg}_2\text{P}_2\text{O}_7$
- No. 3. From 0.4831 gram Florida rock, obtained 0.0333 gram  $\text{Mg}_2\text{P}_2\text{O}_7$
- No. 4. From 1.0036 grams Florida rock, obtained 0.0227 gram  $\text{Mg}_2\text{P}_2\text{O}_7$

<sup>1</sup> To be had from Bullock and Crenshaw, Philadelphia. A disk of filter paper of the diameter of an American silver quarter dollar (fifteen-sixteenths inch) is used, when employing the smallest size funnel. I can highly recommend this funnel in all cases in which the precipitate is to be titrated. The precipitate presents a perfectly flat surface, is easily and quickly washed, and is readily transferred with the aid of the wash bottle to the beaker. The funnel can be employed only when using the suction pump, but it has the advantage of not requiring a platinum cone, and the size of the filter is reduced to a minimum.

<sup>2</sup> Read at the stated meeting of the Chemical Section, of the Franklin Institute held February 20, 1894.

## DETERMINATIONS BY PEMBERTON'S METHOD.

No. 1 used 1.0737 grams  $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$  and 22.88 cubic centimeters KOH solution and 1.85 cubic centimeters acid.

No. 1 used 1.0370 grams  $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$  and 21.30 cubic centimeters KOH solution and 0.80 cubic centimeter acid.

No. 2 used 1.0000 gram Florida rock and 41.85 cubic centimeters KOH and 5.05 cubic centimeters acid.

No. 3 used 1.0000 gram Florida rock and 7.55 cubic centimeters KOH and 3.10 cubic centimeters acid.

No. 4 used 1.0000 Florida rock and 6.75 cubic centimeters KOH and 5.50 cubic centimeters acid.

Strength of  $\text{H}_2\text{SO}_4$  used 1 cubic centimeter = 0.015998 gram  $\text{H}_2\text{SO}_4$ .

Strength of potassium hydroxide solution 1 cubic centimeter = 0.01847 KOH.

The percentages of  $\text{P}_2\text{O}_5$ , calculated from the foregoing determinations, are :

Substance.	Gravimetric. Pemberton.	
No. 1, sodium hydrogen phosphate.....	19.72	19.73
No. 1, sodium hydrogen phosphate.....	19.78	19.99
No. 2, Florida rock.....	37.28	37.22
No. 3, Florida rock.....	4.40	4.53
No. 3, Florida rock.....	4.41	...
No. 4, Florida rock.....	1.45	1.32

It is evident from the above figures that the agreement between the results of the two methods is as close as could be desired. Inasmuch as the Pemberton method is of extreme accuracy, is very easily carried out and effects a great saving of time and labor over the official method, it is well worthy of extended use. We have found that the author's statement of the time required for a single determination, namely, thirty to forty minutes from the time the solution is measured out for titration, is entirely reasonable. Omitting filtration of silica makes no difference in the accuracy of the results.

SWARTHMORE COLLEGE, PA., February 20, 1894.

## THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(Continued from Page 273.)

BY THOMAS B. STILLMAN, PH.D.

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[TO BE CONTINUED.]

## INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

### SUB-COMMITTEE ON METHODS.<sup>1</sup>

#### BULLETIN No. 2.

#### CIRCULAR TO IRON AND STEEL CHEMISTS ON METHOD OF DETERMINING PHOSPHORUS.

AT the World's Congress of Chemists in Chicago a Sub-Committee of the original Committee on International Standards for the Analysis of Iron and Steel was appointed to

<sup>1</sup> The Sub-Committee on Methods for the Analysis of Iron and Steel, have sent the following bulletin to the iron and steel chemists of the country, so far as they could get their names. They earnestly request that any who do not receive a copy of the circular, but who do see this, will comply with the request of the bulletin, the same as though they had received a circular direct.



consider the subject of Standard Methods.

This sub-committee consists of Dr. C. B. Dudley, Chairman, Messrs. A. A. Blair, W. P. Barba, P. W. Shimer, and T. M. Drown. It has recently held a meeting and has decided to recommend standard methods in iron and steel analysis to be used as the basis of commercial transactions. The sub-committee fully appreciates the fact that these methods, to have the highest value, should be in facility and in time of execution such that they will readily recommend themselves for daily use in iron and steel works.

To further this end the sub-committee wishes to have the co-operation of the iron and steel chemists of the country, and to ask them for a brief outline of the processes or methods they use and prefer for the determination of different elements in iron and steel, and for such other information and suggestions as they think will aid it in the work before it. The sub-committee recognizes the fact that it will add immensely to its efficiency and value if the iron and steel analysts of the country will take a personal interest in it, and aid it by their counsel and active influence.

You are therefore requested to send to the chairman of the sub-committee, as soon as convenient, such an outline as you may deem sufficient to fully describe your practice. It is suggested that you follow the general plan here indicated, by answering the following questions, which may be referred to by number to save you unnecessary trouble:

First. What general method do you use for the determination of phosphorus in iron and steel?

Second. What special precautions do you consider necessary to make this method reliable?

Third. What precautions do you take to prevent the interference of arsenic?

Fourth. What factors do you use in your calculations?

Fifth. What variations do you introduce in the case of iron ores or slags?

Sixth. Do you use the same method in pig iron and steel and do you consider the results equally reliable?

Seventh. Do you ever examine the residues insoluble in acid,

in pig irons, or iron ores, and do you ever find phosphorus in them?

Eighth. Are all your determinations made by the same method, or do you check your work by reference to another method, and if so, what method do you use for this purpose?

Ninth. How many determinations do you make a day in your laboratory under ordinary circumstances?

Tenth. What do you consider the greatest length of time necessary to obtain a result, permissible in your work?

The sub-committee begs that you will send at the earliest possible moment as full replies to all or any of the above questions as you conveniently can, and assures you that in making use of any details that may be original with you, you shall have full credit. You will likewise be furnished with copies of the various reports.

CHAS. B. DUDLEY,

APPROVED,

*Chairman Sub-Committee,*

J. W. LANGLEY,

ALTOONA, PA.

*Chairman Com. on Int. Standards.*

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### ERRATUM.

In the column showing percentages for the No. 2 steel on page 219 this number, 0.041 should read 0.048.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### ON THE DETERMINATION OF PHOSPHORIC ACID AS MAGNESIUM PYROPHOSPHATE.<sup>1</sup>

BY HUGO NEUBAUER.

TRANSLATED AND ABSTRACTED BY K. P. McELROY.

**A**FTER giving a brief history of the molybdenum method for the determination of phosphoric acid, Herr Neubauer states his reasons for thinking this method undeserving of its high repute for accuracy. He next gives the results of a long investigation of the sources of error inherent in the method.

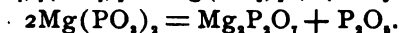
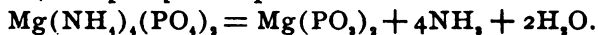
As a standard silver orthophosphate was employed, this salt being chosen partly because of its perfectly definite composition, partly because of the ease with which the base could be estimated. Magnesium ammonium phosphate was rejected for this purpose because it was not thought proper to have the same salt serve as both the beginning and the end. Disodium phosphate was rejected because, of its tendency to absorb carbonic acid. In the first series of experiments on the molybdate method (Wagner's modification), the amount of phosphoric acid found was a trifle less than that known to have been used, the discrepancy ranging from 0.3 mgm. on 84.2 mgms.  $P_2O_5$  to 2.7 mgms. on 166.8 mgms.  $P_2O_5$ . Two explanations could be made of this loss—either that the precipitations were not complete or that volatilization of the phosphoric acid occurred during the ignition of the magnesium salt previous to weighing. Neubauer rejected the former explanation in favor of the latter, adducing a series of

<sup>1</sup> Presented to the World's Chemical Congress, Chicago, August 22, 1893.

experiments in favor of his view. The lid of a platinum crucible was covered with a layer of magnesium hydroxide on the under side and ignited till magnesium oxide was formed and the weight of the lid remained constant. A filter containing magnesium phosphate was then burned in the crucible and after the combustion of the paper, the lid was placed in position and the salt ignited to constant weight. The lid was found to have increased in weight in amounts varying from 0.2 mgm. to 3.8 mgms. The smaller amount was found where the phosphoric acid was directly precipitated and also in a case where magnesium ammonium phosphate reputed to be chemically pure was directly ignited. The largest increase in weight was found in cases where large quantities (five grams) of ammonium chloride or molybdate were added previous to the precipitation of the double phosphate. In the precipitate obtained by the Wagner process (in this method the ammoniacal solution of the yellow precipitate is not neutralized previous to adding the magnesia mixture) the increase varied from 0.5 mgm. to 2.0 mgms. On solution of the magnesia layer on the lid, phosphoric acid was detected by the molybdate reaction. The observation is made that precipitates exposed to the heat of a common Bunsen burner are but little below the truth, while the weights of large precipitates obtained by the molybdate method are often several milligrams too low after strong ignition. The argument is made that the molybdic acid cannot be responsible for this peculiar behavior, since the precipitate when washed till the chlorine reaction disappears contains but an insignificant amount of this substance. Magnesium ammonium phosphate covered before ignition with a weighed amount of lime or magnesia, weighs more than a similar precipitate ignited without this addition, in case an excess of ammonium salts has been present during the precipitation. If the washed precipitate of magnesium ammonium phosphate is dissolved in a very little hydrochloric acid, ammonia in excess added and then two cc. of magnesia mixture, the double precipitated salt will weigh more than it would have done otherwise in case much ammonium molybdate was originally present.

From these facts the conclusion is drawn that in the presence of an excess of ammonium salts, the magnesian precipitate is not

pure dimagnesium ammonium phosphate ( $\text{MgNH}_4\text{PO}_4$ ), but contains more or less monomagnesium ammonium phosphate ( $\text{Mg}(\text{NH}_4)_2(\text{PO}_4)_2$ ). This latter salt decomposes on ignition into magnesium metaphosphate, ammonia, and water. On further ignition, this phosphate becomes converted into pyrophosphate, and phosphorus pentoxide is set free and volatilized.



The greater the concentration of the ammonium salts, the larger the amount of monomagnesium salt which will be formed. For this reason the prevailing ideas relative to the concentration of the solutions to be precipitated are erroneous and more accurate results can be obtained by greater dilution.

Two chances of error exist in the determination of phosphoric acid by the magnesian method—first, that the precipitate may contain too much magnesia, second, that it may contain too little. The second error is readily detected by the method already given. The other may be detected by Tollen's method (*J. Landw*, 1882, 30, 48), which consists in suspending the ignited phosphate in water, adding a little dilute solution of silver nitrate and heating. In the presence of an excess of magnesium, silver orthophosphate is formed and recognized by its yellow color. The reaction is sufficiently sensitive.

Experiments were made with solution of pure magnesium ammonium phosphate containing various amounts of ammonium chloride. In one solution containing 300 mgms. of the chloride, half a milligram of magnesia was found in the filtrate after precipitation by ammonia, and the same quantity of phosphorus pentoxide was volatilized on ignition of the precipitate. In another case where 2.5 grams of ammonium chloride were present, the loss in magnesia and phosphoric oxide were respectively 1.1 and 1.6 mgms. In a third where five grams were employed, the losses were 3.2 and 4.4 mgms. respectively. Finally, phosphoric acid (44.8 mgms.) was precipitated in the presence of 200 cc. of approximately saturated solution of ammonium chloride. The losses reached the large figures of 12.7 and 15.6 mgms. respectively for  $\text{MgO}$  and  $\text{P}_2\text{O}_5$ . The filtrate contained phosphoric acid in amount sufficient to permit its recognition by molybdate, but there was not enough to determine.

Even in the absence of an excess of magnesium chloride the phosphoric acid is wholly precipitated, although ammonium chloride may be present in large amount. The precipitate thus obtained is, however, never of the correct composition. It invariably contains an excess of phosphoric acid and this excess is proportional to the amount of sal ammoniac present. This error is not counteracted by the presence of an amount of magnesium chloride sufficient to form a precipitate of the proper composition.

In the presence of an excess of magnesium chloride the precipitate invariably contains at least enough magnesia to form the normal salt, even in the presence of an excess of ammonium salts. A pure precipitate is, however, only obtained when the amount of free ammonia present is just sufficient for its formation. Any excess of the base causes the precipitate to contain too much magnesia. When ammonia is allowed to slowly flow into a solution containing phosphoric acid and a magnesium salt in excess, the precipitate formed has the normal composition, provided that the rate of flow has been so regulated that the precipitation has taken place in neutral solution. Of course an excess of ammonia must be finally added in order to secure complete precipitation, but this excess is not injurious after the precipitate has once formed.

Various attempts were made to secure a process giving reliable results and yet not too clumsy for practice. Ammoniacal solution of phosphomolybdic acid was neutralized with hydrochloric acid till the yellow precipitate no longer disappeared on stirring and no smell of ammonia could be detected, neutral magnesium chloride solution containing ammonium chloride added, and then dilute ammonia, till a precipitate began to appear. The solution was allowed to stand for awhile, a trifle more ammonia added, and finally, after another wait, an excess of ammonia. By this process correct results were occasionally obtained, but usually the precipitate was a trifle (0.0 to 1.5 mgms.) too heavy and gave Tollen's reaction. For many purposes the results are sufficiently close.

It is probable that in the presence of excess of magnesium chloride and of ammonia some trimagnesium phosphate is

formed, for it is not likely that the excess of magnesia in the precipitate is due to oxide mechanically carried down in the precipitate when quickly formed.

When hydrochloric acid is added to an ammoniacal solution of phosphomolybdate till the precipitate redissolves with difficulty on stirring, the solution reddens blue litmus paper and probably contains free phosphomolybdic acid. On now adding first magnesium chloride in excess and then ammonia, ammonium phosphomolybdate is probably first formed, and then this salt gradually breaks up as more ammonia is added, forming magnesium ammonium phosphate with the magnesia already in solution.

Precipitates obtained from solutions approximately neutral often contain noticeable proportions of molybdic acid in the free state. This is caused by the decomposition of phosphomolybdic acid by ammonia and magnesium chloride. As molybdic acid is not particularly soluble in water, it is deposited simultaneously with the magnesium ammonium phosphate and is enclosed by the latter salt to some extent, and so shielded from the solvent action of the excess of ammonia later added. This separation of free molybdic acid, of course, does not occur in the presence of free ammonia.

The difficulty of preparing the pure double phosphate is not so great in the absence of molybdate and when the excess of magnesium chloride is not large. Washed magnesian precipitates dissolved in hydrochloric acid containing a slight amount of magnesium chloride, and carefully reprecipitated with ammonia, gave better results than had been hitherto obtained. The process is, however, too dependent on the skill of the operator to be reliable.

Magnesium ammonium phosphate can be obtained in three different conditions:

(1) The precipitate is formed in neutral or ammoniacal solution containing no excess of magnesium salt. The result of this is that the precipitate contains less than the normal amount of magnesia, and phosphoric oxide is volatilized on ignition. Therefore weights come out too low.

(2) The precipitate is formed in the presence of an excess of

magnesium salt, but during its formation ammonia is not present in excess. As a result the precipitate possesses the normal constitution and the weights obtained are correct.

(3) The precipitate is formed in the presence of an excess of both ammonia and magnesium salts. The result is that the precipitate contains an excess of magnesia and the weights afforded are consequently too high.

Viewing in the light of these results the method for the precipitation of phosphoric acid (that of Abesser, Jani and Maercker), in which the ammoniacal solution of the yellow precipitate is approximately neutralized with hydrochloric acid, magnesia mixture then added, and subsequently an excess of ammonia, it is readily seen that the following sources of error exist:

A. The whole precipitate is formed as is indicated under (1). This occurs when the amount of ammonia present in the magnesia mixture is so large that precipitation of the phosphoric acid is at once effected when the reagent is slowly added and the liquid stirred, excess of magnesia not being present during the precipitation. Subsequent addition of excess of magnesium chloride or of ammonia is of no avail. The results are similar to those obtained by Wagner's process (in which the neutralization with hydrochloric acid is not practiced).

B. In the formation of the precipitate all three conditions successively occur. This is the case when the amount of ammonia in the magnesia mixture is such that when the reagent is added, drop by drop, stirring constantly, precipitation begins while there is no excess of magnesia, but continues after an excess has been added. Under these circumstances the errors may nearly balance. It is not practicable to form the precipitate wholly of the composition given under (2).

C. When magnesia mixture and ammonia are added drop by drop, stirring constantly, the precipitate formed generally has the composition given under (2) and (3). The 2.5 per cent. ammonia of the usual magnesia mixture is so weak that the precipitate begins to form when magnesia is in excess. The results are consequently too high, and the quicker the precipitation has been effected the higher the results are likely to be, from the



fact that a smaller portion of the precipitate is formed in neutral solution.

D. The precipitate is exclusively of the composition given under (3) only when magnesia mixture and ammonia are too quickly added. The results are in this case even higher than those just referred to under C.

These theoretical conclusions were confirmed by direct experiment.

The common citrate method gives approximate results which is due to the fact that two sources of error counterbalance each other. On the one hand the precipitate invariably contains lime and on the other the phosphoric acid is not completely precipitated. When magnesia mixture is slowly added to an ammoniacal solution of phosphoric acid containing ammonium citrate but no bases forming insoluble salts with phosphoric acid, the precipitate forms mostly in the condition given under (1) and but little in that given under (3), inasmuch as most of it is formed in the absence of an excess of magnesium chloride. This view was confirmed by experiment, but it was also shown that even when the magnesia was rapidly added, some phosphoric acid was volatilized during the subsequent ignition of the precipitate. This is due to the fact that from solutions of phosphoric acid containing no lime salts the precipitate is formed with tolerable rapidity even where citrate was present, so that on the addition of the magnesia mixture a portion of the precipitate is formed in the absence of an excess of magnesium chloride.

The general conclusion drawn from the results of a number of determinations made by various modifications of the molybdate method and by the citrate method is that none of these methods is particularly accurate. It appears practically impossible to completely convert phosphoric acid into pure magnesium pyrophosphate under analytical conditions, where the molybdate method is employed. The exact amount of phosphoric acid in a substance can therefore only be obtained by correcting the results analytically found by a factor, assuming that the errors of analysis are constant for a given amount of phosphoric acid.

Results obtained, where the neutralization with hydrochloric acid is practiced, are oftener nearer the truth than where this

precaution is omitted. However, results thus obtained are dependent on so many sources of error that it is difficult to make parallel analyses. Besides this the method is rather inconvenient. The molybdic acid occurring in the precipitate is a nuisance. Its complete removal by ignition requires skill and practice, and often as much time as the expulsion of the volatile phosphoric acid from the precipitate formed where neutralization is omitted (Wagner's modification). On the other hand the latter modification of the method is very convenient in practice and the attendant relations are so simple, that duplicates must agree where simple precautions are observed.

A systematic determination was made of the errors attendant on Wagner's method and from the results a table constructed, the use of which is recommended for phosphate determinations. The source of error in this method lies exclusively in the loss of phosphoric acid by volatilization. The magnesia-covered crucible lid offers a very good control of this error and its use is recommended to the analyst. Of course, the presence of sulphur in the gas used for ignition is liable to disturb this check.

The following course of procedure in the determination of phosphoric acid can be recommended:

Separate the phosphoric acid in the form of the yellow precipitate and wash this latter in the usual way. Too high a heat should not be employed, nor should the solutions be allowed to stand too long lest excess of molybdic acid separate. Dissolve the phosphomolybdate in 100 cc. of cold 2.5 per cent. ammonia and add as many cc. of the usual magnesia mixture (fifty-five grams magnesium chloride and seventy grams ammonium chloride dissolved in a liter of 2.5 per cent. ammonia) as there are centigrams of phosphoric acid present. Addition should not be made faster than ten cc. per minute. Stir during the addition. After the precipitation stir briskly once more and then allow to stand at least three hours. Wash with 2.5 per cent. ammonia till the chlorine reaction disappears, dry the filter and introduce into a well-cleaned crucible which has been thoroughly ignited. Place the lid at an angle, carbonize the filter and gradually raise the heat, though not higher than a medium red heat, till the pyrophosphate becomes completely white. When

this happens bring the blast into action and ignite to constant weight. The weight finally accepted must not change even after half an hour's ignition. Upon this requirement especial stress must be laid. Pure magnesium pyrophosphate does not suffer any loss even after several hours' ignition, nor does a good platinum crucible. To the weighed amount of pyrophosphate add the correction given in the table. Multiplication of the sum by 64 gives the amount of phosphoric acid in the weight taken for analysis.

## CORRECTION FOR PHOSPHORIC ACID DETERMINATION.

Found, $\text{Mg}_2\text{P}_2\text{O}_7$ , in grams.	Lost, milligrams $\text{Mg}_2\text{P}_2\text{O}_7$ .	Found, $\text{Mg}_2\text{P}_2\text{O}_7$ , in grams.	Lost, milligrams $\text{Mg}_2\text{P}_2\text{O}_7$ .
0.10	0.6	0.24	4.0
0.12	0.8	0.25	4.2
0.14	1.2	0.26	4.6
0.15	1.4	0.27	5.0
0.16	1.6	0.28	5.5
0.17	2.4	0.29	6.1
0.18	2.6	0.30	6.8
0.19	3.2	0.31	7.6
0.20	3.5	0.32	8.6
0.21	3.6	0.33	9.6
0.22	3.8	0.34	10.6

When phosphoric acid is to be estimated as pyrophosphate it must always be first separated as molybdate, even when the original solution contained no bases capable of forming insoluble phosphates, as otherwise these corrections will not be applicable.

Using these corrections, the estimation of phosphoric acid becomes one of the most accurate of known analytical methods.

## EXPERIMENTS ON A FERRO-TUNGSTEN.

BY JAMES S. DE BENNEVILLE.

Received February 28, 1894.

IN making an analysis of a ferro-tungsten rich in tungsten the chemical behavior of a residue insoluble in acids and apparently not decomposed by fused solvents led me to believe that it was metallic tungsten. The time available was limited and the few experiments made were hasty and at intervals, and in a private communication describing the method pursued in analy-

sis I called attention to the insufficient basis on which the analysis rested and the necessity for further investigation. The work involved in this paper was undertaken to determine, if possible, whether tungsten existed uncombined in the alloy and whether any definite ratio between tungsten and iron could be shown or alloys separated. The results showed that what was taken to be tungsten was a rich tungsten alloy the iron of which was not attacked by acids and which in its indifference toward chemical reagents resembled metallic tungsten.

The method of analysis adopted was directed toward determining how different solvents would act on the alloy. The steps taken were from the less to the more energetic reagent and consisted in 1. Attack by strong hydrochloric acid and determination of the iron and tungsten so removed in solution. 2. Fusion of the residue with a mixture of alkali carbonate and nitrate. 3. Action of solution of silver nitrate on the alloy.

The results based on sixteen analyses showed the alloy to be very heterogeneous. The sample was in the form of small fragments showing to the eye the differentiation throughout the mass and even the fragments themselves had not the same appearance, some of them having a number of cleavage planes of a pyritous appearance. In making these later analyses no effort was made to obtain a uniform sample, but the contrary, for the object sought was to ascertain whether all the iron was alloyed with tungsten or *vice versa*; and whether iron and tungsten were present as such dissolved in a true alloy.

A marked regularity was shown in the amount of tungsten dissolved on treating the alloy with ammoniacal silver nitrate solution. However, on digesting with neutral solution of silver nitrate no tungstic acid separated and the silver precipitated was in proportion to the iron dissolved. This absence of tungstic acid from the residue pointed to the fact that all the tungsten was in the form of alloy. The small quantity of iron separated did not calculate to any definite ratio with the tungsten acted on by the silver salt. Part of the iron was probably due to the steel mortar in which, owing to its great hardness, it was necessary to crush the alloy. This would vitiate any calculation.

The results, under I, were obtained by the following method: The fragments of the alloy were powdered separately in a steel mortar and passed through a sixty mesh sieve. Weighed portions were then extracted by strong hydrochloric acid (sp. gr. 1.20) until the acid no longer acted. In this solution iron and tungsten were determined. The residue was fused with a mixture of sodium carbonate and nitrate and the fusion lixiviated in water. Decomposition was complete. Iron and tungsten were determined. The results obtained were as follows:

## I. TO ONE GRAM.

No.	1	2	3	4
Acid extract, iron .....	0.3648	0.3779	0.3631	0.3853
Acid extract, tungsten..	0.0233	0.0309	0.0217	0.0282
Residue, iron.....	0.1786	0.1762	0.1669	0.1416
Residue, tungsten.....	0.4333	0.4057	0.4390	0.4626

Taken in connection with II this table appears to show that part of the alloy is readily attacked by acid, iron being dissolved and the tungsten left behind in the residue. This is indicated by the small quantity of free iron (see II) in the majority of the samples taken for analysis. Any large quantity of unalloyed iron would be shown very positively. This does not show necessarily the separation of an easily decomposed alloy from others less readily attacked. Other facts, given later, indicate that this alloy is an unsaturated compound and that a still higher percentage of tungsten than given in these analyses can be held chemically combined with the iron, but the higher valency exercised by the iron in these rich tungsten compounds may not be the most stable.

It was sought to ascertain how the alloy would act toward silver solution. Four reactions were involved. 1. Metallic iron, reducing silver from its salts in the ratio of Fe:2Ag. The reaction takes place in neutral solution. 2. Metallic tungsten and silver salt in neutral solution. 3. Metallic tungsten and silver salt in ammoniacal solution. 4. Action of the tungsten in this alloy on the silver salt. In the neutral solution of silver nitrate tungsten is converted into tungstic acid and silver is reduced. Silver tungstate is also formed. After washing the precipitated tungstic acid and silver free from excess of silver nitrate and dissolving in ammonia the black silver sulphide was obtained by

ammonium sulphide. The quantity was small but this salt is somewhat soluble in water<sup>1</sup> and washing must have removed some portion of it. The main bulk of the flocculent white precipitate is tungstic acid. In the ammoniacal solution of silver nitrate the tungstic acid formed dissolves leaving silver as residue.

The results obtained from experiments carried out on this line indicated the amount of free iron and by dissolving it out left the residue ready for further treatment. The alloyed ferro-tungsten did not appear to be attacked by the silver nitrate, which was to be expected from the strong affinity of iron for tungsten. In two analyses, however (18 and 19), in which a large quantity of iron replacing silver was found, the tungsten instead of dropping to a low percentage remained near the average found in nearly all the analyses, forty per cent. This looks as if the alloyed ferro-tungsten had been attacked by the reagent, but it can be explained on the ground of segregation. Crookes<sup>2</sup> in criticising Schöffel's method for chrome and tungsten steels by solution of the iron in copper ammonium chloride notes the fact that steels containing a high percentage of chromium (eight per cent.) or tungsten (twelve per cent.) are but slightly attacked.

To make use of the reaction that in ammoniacal solution of silver nitrate tungsten replaces silver in the ratio of  $W : 6Ag$  the following analytical method was adopted:

Weighed portions of the alloy were digested for thirty hours with a neutral solution of silver nitrate. This solution was decanted from the heavy residue and washed by decantation with water. After removal of the excess of silver, iron was determined in this solution giving the quantity of free iron. It was noticeable that in nearly all the analyses this was very small and in part was due probably to fragments from the mortar. In two of the analyses this "free iron" is a considerable percentage of the whole and cannot be put down to that cause. After removal of the neutral silver salt the residue was digested for from thirty-six hours to a week with an excess of ammoniacal solution of silver nitrate. This solution was filtered and the residue

<sup>1</sup> E. F. Smith and Bradbury, *J. Anal. Appl. Chem.*, 5, 486.

<sup>2</sup> Crookes "Select Chemical Methods," pp. 217-219.

washed with water. Silver was removed from the ammoniacal solution by ammonium sulphide and tungsten determined in the filtrate. The residue from the treatment with the silver salt was dried and ignited. Silver was removed by nitric acid and the final residue obtained was fused with a mixture of sodium carbonate and saltpeter. Tungsten was precipitated from the neutral solution of alkali tungstate as mercurous salt. Iron was determined where found. This method of analysis separated the constituents into 1. Iron replacing silver. 2. Tungsten replacing silver. 3. Unattacked iron and tungsten.

The experimental results tabulated were:

III. 9-12 with neutral solution of silver salt; 13-15 with ammoniacal solution of silver salt; 16-20 with neutral and subsequently ammoniacal solution of silver salt.

### III. CALCULATED TO ONE GRAM. ALLOY TREATED WITH SILVER SALT.

No.	Total iron.	Total tungsten.	"Free" iron.	"Free" tungsten.	Residual iron.	Residual tungsten.	A : B less "free" iron ratio.
	A.	B.	C.	D.	E.	F.	G.
9....	0.4068	0.5758	0.0070	....	0.3998	....	7:3
10....	0.4698	0.5081	0.0150	....	0.4548	....	3:1
11....	0.5919	0.3889	0.0072	....	0.5847	....	5:1
12....	0.5199	0.4552	....	0.0453	....	0.4099	..
13....	0.6861	0.2986	....	0.0586	....	0.2400	..
14....	0.6207	0.3700	....	0.0692	....	0.3008	..
15....	0.5118	0.4789	0.0121	0.0399	0.4997	0.4390	0.7:2
16....	0.4075	0.5842	0.0281	0.0522	0.3794	0.5320	0.2:1
17....	0.5227	0.4680	0.0561	0.0367	0.4666	0.4313	3.26:1
18....	0.5221	0.4686	0.3147	0.0626	0.2074	0.4060	3:2
19....	0.4847	0.4933	0.3430	0.0535	0.1444	0.4398	1:1
20....	0.5178	0.4689	0.0150	0.0534	0.5028	0.4155	7:2

The term "free" iron and "free" tungsten is used to indicate the quantity of those metals replacing silver in the silver solution.

The variation in the analytical results appears to show that we have to deal with a number of alloys and these not distributed evenly through the mass. The small quantity of iron replacing silver in silver nitrate indicates that the iron is in combination with the tungsten and not a number of more or less complex alloys dissolved in a matrix of metallic iron. Nos. 18 and 19 can be attributed to segregation on cooling, such segregation taking place when the mass was not very liquid in which case

the separated and unalloyed iron would surround a rich tungsten alloy. Schneider<sup>1</sup> separated from a high tungsten iron what appeared to be two alloys corresponding to the formulas  $\text{Fe}_3\text{W}$  and  $\text{Fe}_2\text{W}$ . If iron be regarded as divalent the saturation point of tungsten would be reached in the formula  $\text{Fe}_3\text{W}$  (taking tungsten as hexavalent). If iron be regarded as octovalent the saturation formula would be  $\text{Fe}_2\text{W}_3$ . Howe in his "Metallurgy of Steel" states that "tungsten unites with iron apparently in all proportions at least up to eighty per cent." The following table of analyses is taken from his work quoted, p. 81:

No.	1.	2.	3.	4.	5.	6.
Tungsten.....	37	77.8	53.1	29.12	24.25	28.18
Iron.....	63	16.4	43.4	67.93	30.	68.36
Manganese ....	..	5.8	3.5	but little	41.50	0.99
Silicon .....	..	....	....	0.61	....	0.23
Carbon .....	..	....	....	1.17	5.65	1.88
Phosphorus ...	..	....	....	....	0.14	0.008

The description given of No. 3, "platinum gray, hard, brittle, lamellar completely fusible" would in the first three qualities apply directly to the ferro-tungsten under consideration. Analysis No. 2 very closely approximates the formula  $\text{Fe}_2\text{W}_3$ , and if no alloy of iron and tungsten, in combination, containing a higher percentage of tungsten, exists, it would point strongly to the octovalency of iron in its combinations with this element as metal. The other analyses, including those of the ferro-tungsten under consideration would be unsaturated compounds. This valency has been shown to belong to other members of this family. Ruthenium and osmium in their oxides, iron in ferric acid, appear as hexavalent and the existence of the ammonia cobalt salts indicate a still higher valency for a metal closely allied to iron.<sup>2</sup>

Mendelejeff compares alloys to solutions as indefinite unstable compounds. In solutions in which there is free communication within the bounds of the liquid on alteration in temperature a change in molecular composition occurs as is shown by the separation of definite salts limited by such temperature. An alloy in the fused state is then analogous to a solution and when during

<sup>1</sup> Howe's Metallurgy of Steel, p. 81.

<sup>2</sup> Lothar Meyer, "Modern Theories of Chemistry," pp. 347, 348.



cooling segregation sets in the different alloys crystallize out from the mass. If the iron were present in such quantity that its saturation capacity for the tungsten would drop below divalency metallic iron would appear in this alloy but this is not the case.

The fact that iron does not replace silver in the silver nitrate or copper in the copper ammonium chloride shows a very strong affinity of iron for tungsten. If the bond between the iron and tungsten atoms was weak, or if there was merely a mechanical mixture, iron should replace silver in the neutral solution of the silver salt. This is based on the fact that "a positive element is separated from its combinations with a negative element by a stronger positive," and iron is more positive than silver.<sup>1</sup> Iron and tungsten are so separated in their properties as metal and semi-metal that an alloy of such constituents should be a very stable compound.

Metallic tungsten is left almost unattacked by hot acid. The action of aqua regia slowly converts it into tungstic acid. The acid must be used in small portions at a time and adhering tungstic acid removed by ammonia to prevent its protective action. Fusion with potassium bisulphate, or with caustic soda, or alkaline carbonate and saltpeter decomposes it.

In its action toward acids the alloy shows very strongly the influence of the tungsten. Acids do not act on it energetically as with carbon steel. To a degree this is to be expected but its inertness is almost as marked as with metallic tungsten. Hydrochloric acid dissolves out about two-thirds of the iron and a little tungsten. Nitric acid does the same. Part of the alloyed iron, therefore, appears to be attacked by acid solvents. Sulphuric acid barely acts upon it but fusion with potassium bisulphate (sulphuric acid at a red heat) decomposes the alloy completely. Aqua regia attacks it slowly but action is soon stopped by the tungstic acid forming a coating which must be removed to obtain further action on the alloy by the solvent. This chemical behavior points to a complex molecular structure. The formula  $\text{Fe}_2\text{W}_4$  is purely empirical and the true formula is probably a very large multiple of this. If the fusibility and volatility of

<sup>1</sup> Modern Theories of Chemistry, pp. 515-517.

compounds diminishes with increasing complexity of structure then in such difficultly volatile metals as tungsten, chromium, platinum, and other metals fusing at high temperatures, and in their alloys, the molecule (in the solid state) must be possessed of large molecular weight and corresponding inertness toward chemical action.<sup>1</sup>

I am indebted to Dr. Wahl, of Philadelphia, through Mr. Garrison, for the material on which these analyses were made.

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### THE DIRECT ESTIMATION OF CITRATE SOLUBLE PHOSPHORIC ACID.

By B. B. ROSS.

Received December 18, 1893.

THE direct determination of citrate soluble phosphoric acid, as is well known, is effected in many European laboratories by precipitating it, as magnesium ammonium phosphate in the presence of the ammonium citrate employed in effecting its solution.

The lack of general applicability, together with other objections, which have been urged against this method, however, has caused its employment to be somewhat restricted and the process has met with little favor in this country.

The presence of the citric acid in the solution has, of course, prevented the direct application of the molybdate method, and several processes have been proposed for the elimination of the citric acid preparatory to the precipitation of the phosphoric acid by the molybdate solution. The writer some years since (Proceedings Association Official Agricultural Chemists, 1885,) proposed the removal of the citric acid by precipitation in the hot solution by means of calcium chloride.

A number of results reported at that time showed quite a close agreement with the figures obtained by the regular official method, but some later tests indicated a loss resulting from the retention of small quantities of calcium phosphate in the precipitate of calcium citrate.

<sup>1</sup> "Modern Theories of Chemistry," pp. 131, 287. Ostwald "Outlines of General Chemistry," pp. 190, 191; in reference to potassium as solid p. 275.

Kuntze (*Ztschr. f. Rübenzucker*, 1892, 860,) recommends for the destruction of citric acid and other organic matters, evaporation of the solution and treatment with sulphuric and nitric acids, followed by thorough ignition. During the past year a number of experiments were made in the laboratory of the Louisiana State University with a view to the elimination of citric acid by means of oxidizing agents by the wet way.

After testing a number of different methods of oxidation it was found that the best and most satisfactory results were to be secured by the employment of the Kjeldahl digestion process. The mode of procedure finally adopted is essentially as follows:

After the completion of the thirty minutes' digestion of the sample with 100 cc. of citrate solution, twenty-five cc. of the liquid are at once filtered out into a dry vessel, preferably into a burette, as the solution can, after cooling, be transferred to another vessel without the dilution attendant upon rinsing the measuring vessel.

Bring the aliquot, thus measured, into a digestion flask of 250 to 300 cc. capacity, add about fifteen cc. concentrated sulphuric acid and place the flask on a piece of gauze over a moderately brisk flame.

Within about eight minutes the liquid will have become quite concentrated and will begin to darken appreciably and at the same time foaming will commence, but will occasion no trouble if an extremely high, or a very low flame be avoided.

After a further lapse of three or four minutes the foaming ceases and the contents of the flask appear quite black; about one gram of mercuric oxide or metallic mercury is now added and the digestion continued over a high flame.

The operation can be readily completed within less than half an hour, and, in many cases, within twenty-five minutes, a clear and almost colorless liquid being obtained.

After cooling, the solution is washed into a beaker, ammonia is added in slight excess, the solution acidified with nitric acid and the regular molybdate method followed, after addition of ammonium nitrate.

In case as large an amount as fifty cc. (corresponding to one gram of the sample) of the filtrate from the citrate treatment is

employed, ten cc. of strong sulphuric acid are at first added and the digestion conducted in a flask of 350 to 500 cc. capacity; after the contents of the flask have blackened and the foaming has progressed considerably, the flask is removed from the flame and fifteen cc. more of sulphuric acid are added and the flask and contents heated with a low flame for two or three minutes; mercuric oxide is next added and the digestion is completed as before described.

Among the chief advantages of this process for the determination of citrate soluble phosphoric acid may be enumerated the following:

1st.—It affords a quick and direct method for the estimation of that form of phosphoric acid which, together with the water soluble, constitutes what is termed "available" phosphoric acid, and the amount of this available phosphoric acid is thus reached by two determinations instead of three according to the ordinary method.

2nd.—The economy of time and labor attendant upon this process gives it an advantage over the indirect method, since by the direct method it is only necessary to filter out twenty-five cc. (or possibly fifty cc.) of the citrate solution, thus obviating the frequently tedious task of filtering the whole liquid and bringing upon the filter and washing with water of a definite temperature the insoluble residue; in addition, the ignition of this residue, the subsequent digestion with acid, dilution to a definite volume and measurement of an aliquot, are operations which are either tedious or time-consuming and can to a large extent be avoided by the use of the direct process.

3rd.—If it is desired, this method can be used as a check or control process in connection with the regular method, the check determination being readily executed without the necessity of weighing a fresh quantity of the sample under examination.

The results of a number of comparative tests of this process and the regular official method are herewith inserted, the principal portions of the work reported having been performed by Mr. R. E. Blouin, assistant chemist, during the past fertilizer season.

The samples tested were ordinary commercial fertilizers and

it will be observed that the agreement in the figures obtained by the two processes is, in the main, quite close.

## RESULTS OF CITRATE-SOLUBLE DETERMINATIONS.

Sample No.		By the direct method.	By difference, (Official method).
1.....		2.16	2.16
" "	2.....	5.63	5.67
" "	3.....	5.37	5.39
" "	4.....	2.44	2.64
" "	5.....	2.00	1.86
" "	6.....	5.40	5.33
" "	7.....	6.90	6.78
" "	8.....	4.55	4.51
" "	9.....	2.75	2.73
" "	10.....	2.04	1.98
" "	11.....	2.07	2.09
" "	12.....	6.46	6.48
" "	13.....	5.24	5.11
" "	14.....	5.12	5.06
" "	15.....	2.87	2.91
" "	16.....	1.61	1.53
" "	17.....	0.37	0.33
" "	18.....	0.94	0.90
" "	19.....	0.33	0.36

In order to further test the reliability of the method, a solution containing phosphoric acid derived from a chemically pure phosphate was employed and phosphoric acid in the aqueous solution was determined by the regular molybdate method; a given quantity of the same solution was next mixed with twenty-five cc. of ammonium citrate solution and after addition of fifteen cc. sulphuric acid, the digestion was conducted as before described and the phosphoric acid determined in the manner previously stated. The results were:

By first method (direct molybdate process) 8.06 per cent.

By second method (addition of citrate solution, etc.) 8.13 per cent.

Other tests with chemically pure salts showed differences which were well within the limits of variation permissible in ordinary analytical work.

Experiments were also made with employment of potassium nitrate in the place of mercuric oxide, but it was found that a number of additions of this substance was required and the time

needed for the completion of the digestion was considerably lengthened.

The Gunning modification of the Kjeldahl digestion process was also tested but the foaming resulting from the employment of the large quantities of potassium sulphate rendered the use of this modification impracticable.

By the employment of either mercuric oxide or metallic mercury, however, the oxidation is effected rapidly and completely and the subsequent precipitation of the phosphoric acid is easily accomplished.

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### NOTES ON THE ESTIMATION OF CRUDE FIBER IN SUGAR CANE.

By J. L. BEESON, PH.D., PROFESSOR OF CHEMISTRY, LOUISIANA SUGAR SCHOOL,  
NEW ORLEANS.

Received February 26, 1894.

THERE is no part of the analytical work connected with the chemical control of diffusion process sugar house so unsatisfactory as that of the estimation of the so-called "crude fiber" in the cane, or that portion of the stalk which is insoluble in water. Duplicate analyses, manipulated with great care, show wide variations. The average of such variations for 100 samples taken consecutively was 0.736 per cent. Since the percentage of fiber is used as a factor in calculating the percentage of sucrose on the weight of the cane it becomes highly desirable that either a better method of fiber estimation be devised, or a more accurate and quick method of estimating the percentage of the sucrose directly on the weight of the cane. After a systematic and thorough investigation of the subject I have come to the conclusion that a very accurate method of fiber estimation for technical purposes is not feasible, on account of the wide variation in fiber content in different parts of the cane stalk.

*Extraction of the Soluble Bodies from the Chips.*—A study was first made of the extraction of the sugars and other soluble bodies in the chips as follows: Twenty grams of chips taken from the comminuter were placed in a beaker, and nine volumes of water of varying temperatures added. The diffusates were polarized every fifteen minutes until the last two readings were the same.

The water in the beakers was kept as nearly as possible at the temperature of the water when added.

Results:

At	23° C.,	diffusion complete in	65 minutes.
"	60° C.,	"	" 45-50 "
"	75-80° C.,	"	" 30-35 "

After pouring off the diffusate as completely as possible the above process was repeated in order to see if there was any appreciable difference in the rate of diffusion for the second application of water, but there was none.

From the polariscope readings of the completely diffused solutions the percentage of extraction of sucrose was calculated for the first two applications of water, and found to be seventy-five to eighty-five per cent. Assuming eighty per cent. for the average of each application of water, and twelve per cent. as the average amount of sucrose in the chips, after five complete diffusions of each sample there would remain in the chips only 0.0384 per cent. of sucrose, which is practically nil. Theoretically, ninety per cent. of the sucrose should be removed for each complete diffusion. In quite a number of cases the final diffusate was tested for sugars by means of the  $\alpha$  naphthol reaction, which invariably showed only a very low percentage of these bodies.

The coagulation point of the water soluble albuminoids by heat was ascertained by gradually raising the temperature of the first diffusates till coagulation began, and found to be between 80 and 90° C. It is therefore unnecessary to begin the extraction by the addition of cold water, then warm water, etc., as is usually done. Since the diffusion is so much more rapid at high temperatures it is advantageous to begin by adding water at 75° C. for the first two diffusions, and boiling water for the last three, letting stand each time for thirty minutes. This can be safely done, as it will be seen, without fear of coagulating the albuminoids. This method was followed throughout the season.

*Losses in the Preparation of the Samples.*—In preparing samples for the estimation of the fiber in different parts of the cane, a portion of a cane stalk cut at the internodes with a sharp knife was rapidly weighed, ten grams cut off from both ends into a tared beaker, and the stalk reweighed, and was found to sus-

tain a greater loss than the ten grams cut off. This process was repeated in four cases, giving similar results.

Results:

No. 1.	Difference in weight after cutting off ten grams,	10.113
" 2.	" " " " " " " "	10.161
" 3.	" " " " " " " "	10.100
" 4.	" " " " " " " "	10.102

The chips were cut off in semi-circular pieces about  $\frac{1}{8}$  of an inch in diameter. Sample 1, as soon as weighed, was cut finer with a pair of sharp scissors and rapidly weighed. It sustained a further loss of 0.107 gram, which added to the first loss makes a total of 0.22 per cent. while preparing the sample. These losses could not have been due in the main to evaporation, for the whole time occupied in preparing sample No. 1 was not over twenty minutes. Then Nos. 2, 3, and 4, were cut off early in the morning when the samples of 10 grams each lost by evaporation, for one hour, on an average 0.079 gram. The loss was more likely a mechanical one of the juice due to the rupture of the cells by the knife while cutting off the chips. If so, this loss would be augmented by the cutter and comminuter in the mill, especially so when the knives are dull.

*Loss by Evaporation from the Chips.*—According to well-known laws of physics the amount of evaporation varies with time of exposure, surface area exposed, and the temperature and humidity of the atmosphere. The fineness of the chips, which increases the surface, affects the rate of evaporation, probably also the ratio of the juice to the fiber. Upon the latter point I made no experiments. A piece of cane stalk, about an inch in diameter, was cut at the internodes, weighed, placed in the shade and reweighed at the end of each hour. The temperature at 12 o'clock 78° F., day dry.

Results:

12-1 P. M.,	loss by evaporation.....	0.48 gram.
1-2	" " " " .....	0.56 "
2-3	" " " " .....	0.40 "
3-4	" " " " .....	0.49 "
4-5	" " " " .....	0.52 "
Average loss each hour.....		0.49 gram.

This evaporation was mainly from the open ends and is therefore largely independent of the length of the piece of stalk.



Ten grams of chips were placed in a beaker in the room and weighed every hour, with the following results:

No. 1.	From 10.30-11.30 A. M.,	loss by evaporation,	0.086 gram.
" 2.	" " " " " "	" " " "	0.073 "
" 1.	" 11.30-12.30 " " "	" " " "	0.269 "
" 2.	" " " " " "	" " " "	0.266 "

The morning was very damp, there being a heavy fog which did not clear away until nearly 10 o'clock. From these results it would appear that quite an error may come from evaporation of the chips while the samples are accumulating at the mill, which often requires an hour or more. Add to this the mechanical loss from cutting the chips by the machine, and the error is sufficient to make the fiber appreciably high.

*The Distribution of Fiber in the Cane.*—These sources of error do not, of course, account for the differences in duplicate analyses. This error must be sought for in the difficulties in obtaining an average sample—in the variation in the fiber content in the different parts of the cane. To this end the following analyses were made: Ten grams of fiber were cut from the nodes, and ten grams from the contiguous internodes of the top, middle and butt of a stalk of purple cane, third year stubble of average size and weight, and the fiber estimated in these portions, giving the following results:

Top {	Node..... 15.86 per cent.	Middle {	Node..... 15.9 per cent.
	Internode 8.60 " "		Internode 8.0 " "
Butt {	Node..... 18.20 per cent.		
	Internode 8.08 " "		

It will be noticed that there is approximately twice the percentage of fiber in the nodes as in the internodes, the butt node showing the highest percentage.

Fiber content in the rind and pulp of portions of cane stalk taken from the top, middle, and butt, cut so as to include a node and internode. (a) purple variety, plant cane; (b) purple variety, third year stubble.

	Rind.	Pulp.		Rind.	Pulp.
(a) Top.....	26.0	8.7	(b) Top.....	25.6	7.80
Middle ..	29.5	6.5	Middle..	28.5	5.40
Butt .....	28.5	6.8	Butt.....	28.5	5.77

Stubble cane always has a higher fiber content than plant cane of the same variety. From the above it would appear that this difference resides more in the pulp than in the rind.

It is difficult to say just what is rind and what is pulp in the cane stalk. So a portion of cane, about five inches in length, was cut from the center of a stalk of plant cane, purple variety, just within the two nodes. Ten grams of the rind was pared off into one beaker, ten grams taken off all round from what remained, and so on until the center of the stalk was reached, and the fiber estimated in these separate portions with the following results:

True rind .....	33.9	per cent.
Inside rind or bast tissue .....	13.33	" "
Next to inside rind .....	6.79	" "
Next to middle .....	4.77	" "
Middle .....	4.13	" "

The diffusate from the inside bark (bast cells?) was quite yellow, and it is probable that these cells furnish the yellow coloring matter in the expressed juice.

A joint of cane was cut just without the nodes, and the true node separated from that portion penetrated by the rootlets of the eye. Then ten grams were cut off from both ends of what remained at right angles to the length of the stalk, and an average of what remained was taken, and the fiber estimated in these portions, with the following results:

PURPLE VARIETY, THIRD YEAR STUBBLE.

Nodes proper .....	21.3	per cent.
Root nodes .....	14.2	" "
Next to the above .....	14.13	" "
Remaining internode .....	11.9	" "

From the above data it will be seen that the fiber varies very widely in amount in different parts of the cane, from 4.13 per cent. in the pulp to 33.9 per cent. in the rind. The percentage of what was considered as rind in the above analyses was estimated, and as an average of four cases was approximately twenty-one per cent. the weight of the cane. With such a difference in the fiber content of the rind and pulp, and such a percentage of rind, it is no small wonder that the duplicate analyses could not be brought to agree. For the presence of a very small undue proportion of rind or pulp in the samples would make the duplicates disagree. Often the knives of the cutters are dull, and strips of rind, varying in length, get into the chips. These, by the motion of the carriers, tend to accumulate on top, and are easily gotten hold of in undue proportion in the taking of the

sample. In such cases it is more difficult to get an average sample than when the chips are fine and regular.

## LOSS OF GOLD AND SILVER DURING SCORIFICATION ASSAY.

BY W. P. MASON AND J. W. BOWMAN.

Received October 6, 1893.

NO explanation of the following numerical results is required, beyond stating that the losses referred to represent total losses, that is to say, losses due to both volatilization and mechanical causes. The furnaces employed were "Battersea No. F," and the conditions under which the assays were made, such as heat of muffle, draught in muffle, and manipulations in general, were such as would obtain in careful practical work.

SILVER.				GOLD.			
Weight before cupelling.	Weight after cupelling.	Loss.	Per cent.	Weight before cupelling.	Weight after cupelling.	Loss.	Per cent.
210.765	206.360	4.405	2.09	338.030	335.025	3.005	0.888
543.165	535.645	7.52	1.38	349.020	348.200	0.820	0.234
206.360	200.325	6.035	2.92	335.025	334.365	0.660	0.197
535.645	523.330	12.315	2.29	348.200	346.900	1.30	0.373
200.325	196.720	3.605	1.79	334.365	333.120	1.245	0.372
523.330	514.765	8.565	1.63	346.900	345.790	1.11	0.319
196.720	191.733	4.987	2.53	332.575	331.725	0.85	0.255
514.765	503.950	10.815	2.10	345.790	344.15	1.64	0.474
191.733	187.820	3.913	2.03	331.725	330.600	1.125	0.338
434.180	424.925	9.255	2.13	344.965	344.265	0.70	0.202
187.820	184.525	3.295	1.80	330.600	329.900	0.70	0.211
424.925	419.975	4.95	0.95	334.650	343.960	0.69	0.206
184.525	180.560	3.965	2.14	329.900	329.130	0.77	0.233
419.975	410.430	9.545	2.27	220.635	220.200	0.435	0.197
410.430	403.365	7.065	1.72	329.130	328.860	0.27	0.082
403.365	394.550	8.815	2.18	220.200	219.835	0.365	0.165
Average loss..... 1.99 per cent.				Average loss..... 0.296 per cent.			
"	"	entire process.. 2.54	" "	"	"	entire process 0.87	" "
"	"	by cupellation.. 1.99	" "	"	"	by cupellation 0.296	" "
"	"	in scorification. 0.55	" "	"	"	in scorification 0.574	" "

SILVER.				GOLD.			
Weight before scorifying and cupelling.	Weight after scorifying and cupelling.	Loss.	Per cent.	Weight before scorifying and cupelling.	Weight after scorifying and cupelling.	Loss.	Per cent.
466.850	453.200	13.65	2.92	357.750	351.982	5.768	1.61
480.052	469.575	10.477	2.18	388.525	382.565	5.960	1.53
455.00	434.365	20.635	4.53	353.782	346.234	7.548	2.10
471.375	456.475	14.9	3.16	384.365	382.033	2.332	0.60
436.165	425.780	10.385	2.38	348.034	346.325	1.709	0.49
458.275	448.818	9.457	2.06	383.833	381.875	1.958	0.51
427.580	418.533	9.057	2.11	348.125	346.435	1.690	0.48
652.350	641.520	10.83	1.66	478.120	471.920	6.2	1.29
354.200	344.520	9.68	2.73	348.235	346.250	1.985	0.57
643.320	628.175	15.155	2.35	473.720	471.225	2.495	0.52
346.320	340.500	5.82	1.68	348.05	346.465	1.585	0.45
614.920	600.565	14.355	2.33	356.425	352.435	3.99	1.11
342.300	333.075	9.225	2.69	348.265	345.535	2.73	0.78
602.365	592.200	10.165	1.68	354.235	352.525	1.71	0.48
334.875	327.140	7.735	2.30	347.335	345.800	1.535	0.44
594.000	581.465	12.535	2.11	354.325	352.075	2.25	0.63
328.84	317.83	11.11	3.37	347.600	344.135	3.465	0.99
567.62	555.365	12.255	2.15	353.875	350.925	2.95	0.83
219.450	210.765	8.685	3.95	221.635	219.25	2.385	1.07
557.165	543.165	14.000	2.51	352.725	349.02	3.705	1.05
Average percentage loss.....2.54 per cent.				Average percentage loss.... 0.87 per cent.			

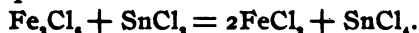
RENSSELAER POLYTECHNIC INSTITUTE,  
1893.

## ON THE SPEED OF REDUCTION OF FERRIC CHLORIDE BY STANNOUS CHLORIDE.

BY LOUIS KAHLENBERG.

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THE reaction that takes place when ferric chloride is treated with stannous chloride in aqueous solution is expressed by the following equation :



This reaction goes on slowly enough at ordinary temperatures to admit of study from the standpoint of chemical dynamics. It was my purpose to investigate whether the reaction proceeds

in accordance with the law of mass action, as stated by Guldberg and Waage,<sup>1</sup> and how the speed of the reaction is affected by the presence of varying quantities of free hydrochloric acid.

*Outline of Method of Experimentation.*—Solutions of ferric chloride and stannous chloride of known strength were prepared. These were brought to a definite temperature by allowing them to stand in a bath. They were then quickly mixed (in equivalent proportions), and the mixture was kept at the same temperature in an atmosphere of carbon dioxide. At convenient times, samples were taken out with a pipette; these were quickly run into an excess of a saturated solution of mercuric chloride, which, by converting the unchanged stannous chloride into stannic chloride, according to the equation,  $\text{SnCl}_2 + 2\text{HgCl}_2 = \text{SnCl}_4 + 2\text{HgCl}$ , checked the reaction. The amount of ferrous chloride formed was then determined by means of a standard solution of potassium bichromate. In this process, the bichromate was added until a drop of the mixture on a white porcelain plate showed no longer a blue coloration when brought into contact with a drop of a dilute, freshly prepared solution of potassium ferricyanide.

*Preparation of Solutions.*—A decinormal solution of potassium bichromate was prepared by taking 4.913 grams of the pure salt to a liter. Its strength was verified by comparison with both ferrous ammonium sulphate and iron wire. 17.85 cc. of this solution will change 0.1 gram of iron from the ferrous to the ferric state.

The ferric chloride used was of Merck's manufacture (C. P.). It was tested for arsenic and for sulphuric, nitric, and free hydrochloric acid, and found pure. Four liters of ferric chloride solution were prepared. The strength of this solution was determined by means of the decinormal bichromate solution, after previous reduction at a boiling heat with a slight excess of stannous chloride, and addition of an excess of mercuric chloride before titrating.<sup>2</sup> It was found that twenty-five cc. of the ferric chloride solution were equivalent to twenty-eight cc. of the bichromate.

<sup>1</sup> *Études sur les affinités chimiques*, 10, Christiania, 1867; also *J. prakt. Chem.*, [2], 19, 69.

<sup>2</sup> Kessler, *Pogg. Ann.*, 95, 223-225; also *Ztschr. anal. Chem.*, 11, 249.

Banca tin was used in preparing the solution of stannous chloride. The tin was found to be free from lead, iron, and arsenic. 30.5 grams of tin, to which a few scraps of platinum had been added, were heated with 125 cc. of hydrochloric acid of sp. gr. 1.17 in a flask in an atmosphere of carbon dioxide until nearly all the tin was dissolved. The heating had to be continued for about six hours. A little distilled water, previously boiled, was added from time to time so as to keep the volume of the liquid at about 100 cc. When the chemical action had ceased, about four to five grams of tin still remained undissolved. The excess of hydrochloric acid was driven off by boiling the liquid down to a small bulk. The stannous chloride thus obtained was diluted to 4,000 cc. with water previously boiled and cooled in an atmosphere of carbon dioxide. That the free hydrochloric acid had been driven off was evident from the fact that a precipitate of stannous oxychloride formed by diluting to this volume. It was found necessary to add to the four liters twenty cc. of hydrochloric acid, of sp. gr. 1.17, to bring this precipitate into solution. After this addition of acid and thorough shaking there still remained a faint opalescence, showing that a minimum quantity of acid had been used. The solution thus prepared was at once transferred to a number of flasks holding from 225 to 250 cc., about the quantity required for each series of experiments. The flasks were completely filled with the liquid, then tightly corked and kept in the dark. In this way the stannous chloride solution could be kept for weeks without changing, and the required quantity could be taken for use without exposing the remainder to the oxidizing influence of the air. The strength of the stannous chloride solution was determined as follows: Twenty-five cc. of the ferric chloride were acidified with hydrochloric acid and heated to boiling, twenty cc. of the stannous chloride were then quickly added and the amount of ferrous chloride formed at once estimated with the decinormal bichromate solution. In this way it was found that twenty cc. of the stannous chloride would reduce 18.7 cc. of the ferric chloride.

A saturated solution of mercuric chloride was also prepared.  
*Experimental Details.*—In each of the six series of experiments

conducted, 200 cc. of the solution of stannous chloride and 187 cc. of the ferric chloride solution were used. The volume of this mixture was made up to 425 cc. for each series. In series I this was done by adding thirty-eight cc. of water, while in series II to VI, five, ten, fifteen, twenty, and twenty-five cc. of hydrochloric acid, of sp. gr. 1.17, at 20° C. respectively were added, together with an amount of water sufficient to make the volume up to 425 cc.

Preliminary experiments had shown that the speed of the reaction is greatly increased by raising the temperature and by increasing the amount of free hydrochloric acid present. The experiments were consequently carried out at 0° C., in order that the reaction might go on slowly enough to admit of the study of the increase of the speed of the reaction by the presence of the amounts of free hydrochloric acid above mentioned.

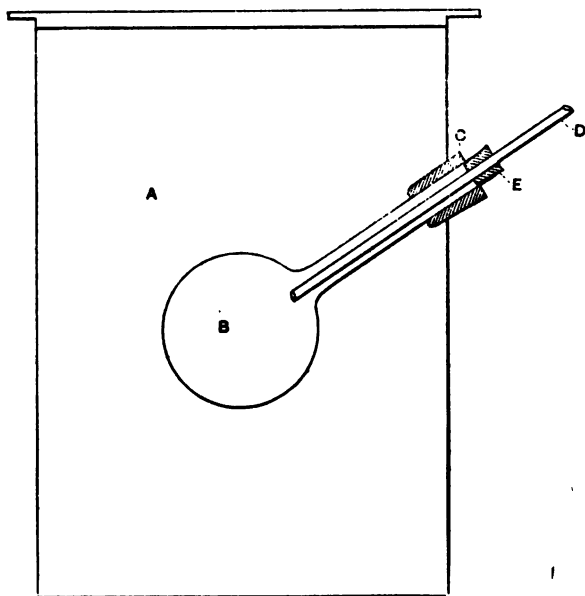


FIGURE 1.

Fig. 1 shows the apparatus in which the mixture of stannous chloride and ferric chloride was kept at 0° C. and in an atmosphere of carbon dioxide. The outer vessel A is made of tin and

has a capacity of about sixteen liters. It is provided with a wooden jacket and cover. The flask B has a capacity of about 500 cc. It is held in position by the tightly fitting rubber cork C which fits closely into the spout with which A is provided. The cork E fits loosely into the neck of the flask. The tube D is connected with a carbon dioxide generator.

At the beginning of each series of experiments, A was completely filled with melting ice and the air in the flask displaced by carbon dioxide. In the meantime the 200 cc. stannous chloride solution and the 187 cc. of ferric chloride solution, plus the thirty-eight cc. water—or water plus acid—were cooling in separate flasks in a bath of melting ice. When the solutions had been cooled to 0° C., they were quickly mixed and poured into the flask B, Fig. 1, the cork E being at once replaced. Samples of twenty-five cc. each were then taken out with a pipette from time to time, the cork E being slightly raised for the moment so that the pipette could be introduced into the flask B. These samples were quickly run into Erlenmeyer flasks containing fifteen cc. of the saturated mercuric chloride solution. The ferrous chloride formed was then estimated by means of the decinormal solution of potassium bichromate, the end of the reaction being judged as above stated. The results of the six series of experiments are given below.

*Presentation of Results.*—In accordance with the law of Guldberg and Waage, the speed of the reduction of ferric chloride by stannous chloride, when the substances are present in equivalent proportions, is to be expressed by the following equation:

$$\frac{dx}{dt} = c(a - x)^2, \quad (1)$$

in which  $a$  represents the amount of substance present at the outset,  $x$ , the amount of substance changed during the time,  $t$ , and  $c$ , a constant depending on the concentration, temperature, etc.

From the above equation we have by integration:

$$\frac{1}{a - x} = ct + K. \quad (2)$$

Determining  $K$  from the fact that  $x$  is zero when  $t$  is zero, and substituting its value in (2), we have after easy transformation,



$$\frac{1}{t} \frac{x}{a-x} = ac. \quad (3)$$

The condition then that must be fulfilled, if the reaction follow the law, is that  $ac$  be constant.

The results of the six series of experiments are given in tabular form. Under  $t$  is given the time in minutes, counted, in the case of series I to V, from ten minutes after mixing the substances; while in series VI, five minutes after mixing was taken as the zero point from which to count the time. In the second column are given the amounts of the decinormal bichromate solution used in estimating the ferrous chloride formed. In series I the results of the titrations of two independent series of experiments are given under 1 and 2, while the average is given under 3. The last three columns of each series give the values of  $x$ ,  $\frac{x}{a-x}$ , and  $ac$ , respectively.

For purposes of comparison, the results given in series I to VI have also been charted in the form of curves—Fig. 2. The abscissae represent the time in minutes, counting from the time of mixing, and the ordinates represent the amounts of ferric chloride reduced in percentages of the total amount present at the beginning. The numbers of the curves correspond to the numbers of the series.

SERIES I. (No free HCl present.)

t (minutes.)	$K_2Cr_2O_7$ (cc.)			x	$\frac{x}{a-x}$	ac.
	1	2	3			
0.....	1.3	1.25	1.27	...	.....	.....
10.....	2.1	2.3	2.2	0.93	0.0921	0.00921
20.....	2.9	2.8	2.85	1.58	0.1672	0.00836
40.....	3.7	3.7	3.7	2.43	0.2825	0.00706
60.....	4.2	4.2	4.2	2.93	0.3617	0.00603
80.....	4.8	4.6	4.7	3.43	0.4513	0.00564
100.....	5.25	5.2	5.23	3.96	0.5601	0.00560
120.....	5.6	5.6	5.6	4.33	0.6462	0.00539
140.....	6.0	6.0	6.0	4.73	0.7508	0.00536
190.....	6.6	6.4	6.5	5.23	0.9017	0.00475
250.....	7.25	7.3	7.27	6.00	1.1928	0.00477
320.....	7.6	7.6	7.6	6.33	1.3468	0.00421

( $a = 11.03$ )

## SERIES II. (Five cc. HCl present.)

t (minutes.)	$K_2Cr_2O_7$ (cc.)	x	$\frac{x}{a-x}$	ac.
0.....	2.95	...	.....	.....
10.....	4.45	1.50	0.1911	0.01911
35.....	6.55	3.60	0.6261	0.01789
50.....	7.1	4.15	0.7981	0.01596
70.....	7.6	4.65	0.9894	0.01413
80.....	7.95	5.00	1.1494	0.01437
110.....	8.5	5.55	1.4605	0.01327
140.....	8.95	6.00	1.7910	0.01279
170.....	9.3	6.35	2.1166	0.01245

(a = 9.35)

## SERIES III. (Ten cc. free HCl present.)

t (minutes.)	$K_2Cr_2O_7$ (cc.)	x	$\frac{x}{a-x}$	ac.
0.....	5.55	...	.....	.....
10.....	7.1	1.55	0.2981	0.0298
20.....	7.95	2.40	0.5517	0.0276
30.....	8.5	2.95	0.7763	0.0259
40.....	8.95	3.40	1.0149	0.0254
50.....	9.2	3.65	1.1778	0.0236
70.....	9.65	4.10	1.5094	0.0216
100.....	9.95	4.40	1.8734	0.0187
120.....	10.15	4.60	2.1394	0.0178
150.....	10.45	4.90	2.6487	0.0177

(a = 6.75)

## SERIES IV. (Fifteen cc. free HCl present.)

t (minutes.)	$K_2Cr_2O_7$ (cc.)	x	$\frac{x}{a-x}$	ac.
0.....	7.1	...	.....	.....
10.....	8.5	1.4	0.368	0.0368
20.....	9.25	2.15	0.705	0.0352
30.....	9.7	2.6	1.000	0.0333
40.....	10.05	2.95	1.311	0.0328
50.....	10.35	3.25	1.667	0.0333
70.....	10.6	3.5	2.059	0.0292
80.....	10.75	3.65	2.355	0.0294
90.....	10.85	3.75	2.586	0.0287

(a = 5.2)

## SERIES V. (Twenty cc. free HCl present.)

t (minutes.)	$K_2Cr_2O_7$ (cc.)	x	$\frac{x}{a-x}$	ac.
0.....	7.55	...	.....	.....
10.....	9.15	1.6	0.508	0.0508
21.....	9.95	2.4	1.021	0.0486
50.....	10.8	3.25	2.167	0.0433
70.....	11.1	3.55	2.958	0.0423
95.....	11.35	3.8	4.000	0.0421

(a = 4.75)

## SERIES VI. (Twenty-five cc. free HCl present.)

t (minutes.)	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (cc.)	x	$\frac{x}{a-x}$	ac.
0.....	7.05	...	....	.....
10.....	9.25	2.2	0.721	0.0721
20.....	10.15	3.1	1.442	0.0721
25.....	10.40	3.35	1.763	0.0705
35.....	10.75	3.7	2.387	0.0682
50.....	11.00	3.95	3.038	0.0608
70.....	11.25	4.2	4.000	0.0571
100.....	11.45	4.4	5.176	0.0518
130.....	11.55	4.5	6.081	0.0468

(a = 5.25)

It will be noticed that the quantity ac, instead of being constant, decreases in each series. In eight preliminary series of experiments, performed at 0° and at 15° to 16°, the same regular decrease of ac was noted. The cause of this retardation of the speed of the reaction has not been further investigated. It seems probable that it is due to the accumulation of the products of the reaction (stannic chloride and ferrous chloride), and to the change in the rate of diffusion as the solution becomes more dilute. It must be observed, however, that while the first values of ac in each of the six series given above are too high, owing probably to disturbing influences at the beginning of the experiments, the values at about the middle of the series vary but slightly indeed, in many instances the differences fall within the limit of error of experimentation. The results above given are sufficient to show that the reaction follows the law of Guldberg and Waage fairly well.

The effect of the presence of varying quantities of free hydrochloric acid on the speed of the reaction can best be seen by comparing the curves in Fig. 2. All the curves show that the reaction goes on most rapidly during the first ten to fifteen minutes after mixing.<sup>1</sup> During the first forty minutes after mixing, the second five cc. hydrochloric acid (curve III) increases the amount of ferric chloride reduced in about the same degree as does the first five cc. (curve II); but this effect diminishes relatively as the time increases. In general, the curves show that as the amount of free hydrochloric acid is increased the effect on

<sup>1</sup> This effect has in part been eliminated in preparing the tables above, by choosing ten minutes after mixing as the zero point from which to count the time.

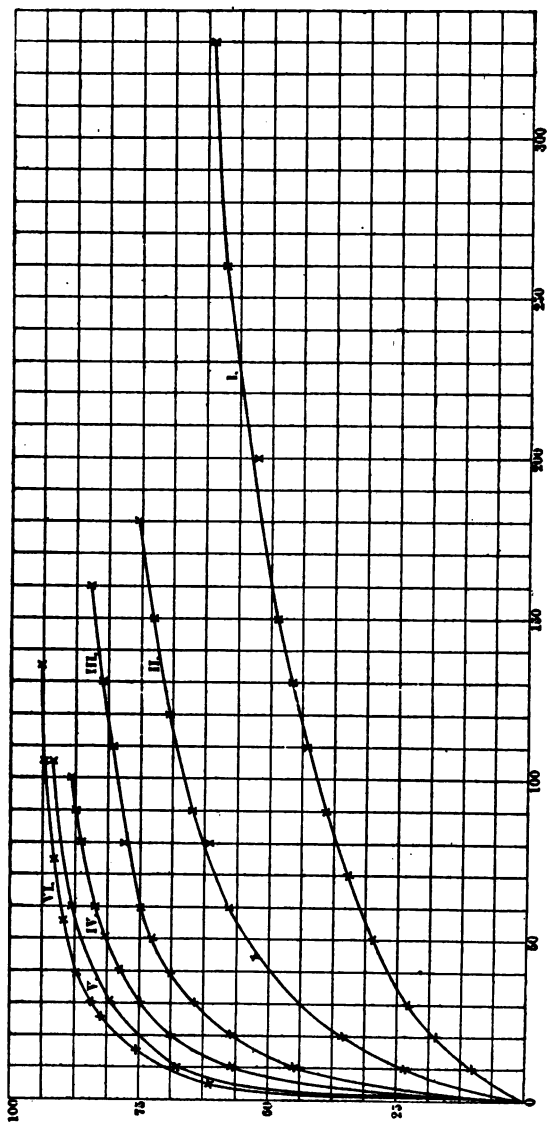


FIGURE 2.

Abscissae = Time in minutes.  
 Ordinates = Amount of  $\text{FeCl}_3$  reduced in per cent.  
 Curve I, no free  $\text{HCl}$  is present.  
 " II, 5 cc. free  $\text{HCl}$  is present.  
 " III, 10 " " " "  
 " IV, 15 " " " "  
 " V, 20 " " " "  
 " VI, 25 " " " "

amount of ferric chloride reduced is relatively diminished.

Curves similar to those in Fig. 2 have lately been obtained by Seubert and Dorrer<sup>1</sup> in the case of the action of ferric chloride on potassium iodide. Their curves show the effect of the presence of an excess of either substance on the speed of the reaction.

In the case of the reduction of ferric chloride by stannous chloride, the part played by the free hydrochloric acid cannot be expressed in the form of a chemical equation; and as there can be no doubt that the amount of free acid present at the end of the reaction is the same as at the beginning, the action of the acid is catalytic in its nature. In the course of his investigations of processes of oxidation and reduction, Prof. Ostwald<sup>2</sup> has formulated the law that the speed of all processes of oxidation and reduction is increased by the presence of free acids in proportion to their affinity coefficients. He has shown that this law holds also in cases of catalytic action. It would be of interest in this connection to know the effect of the presence of equivalent quantities of other acids on the speed of the reduction of ferric chloride by stannous chloride; but as another problem required my immediate attention, the work could not be continued in this direction.

My thanks are due to Prof. W. W. Daniells for occasional helpful suggestions during the progress of the above experiments.

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## THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(Continued from Page 286.)

BY THOMAS B. STILLMAN, PH.D.

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<sup>2</sup> *Ztschr. phys. Chem.*, 2, 127.

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[TO BE CONTINUED.]

## CREAM OF TARTAR SUBSTITUTES: THEIR CHEMISTRY AND ANALYSIS.

BY W. E. WADMAN.

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TO make an intelligent analysis of any complex substance, the chemist must possess not only the requisite skill, but also a certain amount of knowledge of the material he is working with, in order that the bare analytical results may be correctly interpreted, and given their proper meaning in relation to the particular substance yielding them.

Among the substances with which the majority of practicing chemists appear to be little familiar, is the class of products known in trade under the generic name of cream of tartar substitutes.

Under this general name are included a great many acid powders which are used to replace cream of tartar in the manufacture of baking powders, self-raising flours, and also directly in baking, their function being always that of an acid to liberate carbonic acid gas from sodium bicarbonate.

All cream of tartar substitutes have the common feature that their active acid element is primarily monocalcium phosphate, ( $\text{CaH}_2\text{P}_2\text{O}_8$ ), but in other respects they differ so widely in composition and function, that for convenience in considering them it is best to divide them into two primary classes or types.

The first class (hereafter referred to as class I) consists of goods prepared by treating calcium phosphate (in practice usually in the form of boneblack) with sufficient sulphuric acid to produce monocalcium phosphate and calcium sulphate, filtering off the sulphate, evaporating the solution of monocalcium phosphate to crystallization, mixing with starch, drying and grinding. The resulting product is chiefly a mixture of monocalcium phosphate with starch, but invariably contains a small amount of "free" or uncombined phosphoric acid (varying from one per cent. to six per cent.  $\text{P}_2\text{O}_5$ ), and also a considerable quantity of insoluble phosphates, chiefly calcium but frequently iron and aluminum phosphates also. Tartar substitutes of this class are frequently known in trade as "Leached goods."

The other primary type (hereafter referred to as class II) differs from the preceding in method of manufacture, in chemical composition and also in its use and behavior.

The raw material is carefully prepared, pure white bone ash which is treated with the requisite amount of concentrated sulphuric acid, and the resulting mixture, monocalcium phosphate and calcium sulphate, is dried and ground without separation. Hence goods of this type contain a large amount of calcium sulphate, equivalent to the amount of sulphuric acid used in their preparation, and are frequently referred to as "sulphate of lime base" goods.

The essential difference between the two principal types is, that one is practically free from calcium sulphate, while the other contains a large amount of this salt.

Like class I the goods of the second class almost always contain a small amount of free phosphoric acid, and generally considerable quantities of insoluble phosphate, chiefly tricalcium. As a rule they contain very little starch, and frequently none at all.

With regard to this content of calcium sulphate in goods of the second class, it is a common mistake of chemists who are not familiar with these materials, to stigmatize it as an "adulteration," or "the result of careless or imperfect manufacture." Such statements are entirely erroneous, as the calcium sulphate is an essential part of the goods and has a very important influence on their action, as explained later.

A point to be noticed, which is a stumbling block to many chemists, is the simultaneous occurrence of free phosphoric acid and insoluble phosphates. It is usually supposed that these two substances in contact will at once react to produce monocalcium phosphate ( $\text{Ca}_3\text{P}_2\text{O}_8 + 4\text{H}_3\text{PO}_4 = 3\text{CaH}_2\text{P}_2\text{O}_8$ ) and I have seen the statement, over the name of a well-known chemist, that "free phosphoric acid and insoluble phosphates cannot exist together." As a matter of fact the above reaction, like many others, is seldom, and only under exceptional circumstances, complete, and free phosphoric acid and insoluble phosphates not only can, but almost invariably do co-exist in tartar substitutes. This fact has an important bearing on the analysis of these substances.



As examples of the composition of the two extreme types above described, the following analyses may be given:

	Class I.	Class II.
Moisture .....	4.41	2.42
Monocalcium phosphate (crystallized).....	49.67	29.48
Monomagnesium phosphate (crystallized).....	2.75	3.54
Free phosphoric acid (hydrated).....	2.02	0.73
Insoluble calcium phosphate.....	13.08	8.66
Calcium sulphate (anhydrous).....	0.85	48.70
Silica, etc. ....	0.3	0.13
Starch .....	26.00	3.27
Alkaline salts, water of crystallization, and unde- termined .....	0.92	3.07
	<hr/> 100.00	<hr/> 100.00

100 lbs. will neutralize sodium bicarbonate..... 45 lbs. { cold  $27\frac{1}{2}$   
hot  $48\frac{1}{2}$

There are many grades in the market intermediate between these, prepared for special uses, but which may practically be regarded as mixtures of these two principal types.

#### EFFECT OF CHEMICAL COMPOSITION ON THE CHARACTER AND PRACTICAL BEHAVIOR OF THE GOODS.

*Class I.*—The acidity or neutralizing power of this class is entirely due to the monocalcium phosphate and the free phosphoric acid, the exact nature of the reaction with soda varying with the conditions of temperature, dilution, etc., etc., but mainly resulting in the production of dicalcium phosphate  $\text{Ca}_2\text{H}_2\text{P}_2\text{O}_7$  and disodium hydrogen phosphate.

Both monocalcium phosphate and phosphoric acid being readily soluble substances, the reaction takes place practically to the same extent in hot or cold solution.

With goods of the second class, *i. e.*, containing calcium sulphate, the reaction with soda is quite different. The primary reaction of the monocalcium phosphate on the sodium bicarbonate is the same as in the foregoing, but on heating, a secondary reaction occurs between the calcium sulphate and the products of the primary reaction, probably thus:  $3\text{Na}_2\text{HPO}_4 + 3\text{CaSO}_4 = \text{Ca}_3\text{P}_2\text{O}_7 + 3\text{Na}_2\text{SO}_4 + \text{H}_2\text{PO}_4$ , which it will be seen, is equivalent to liberating a fresh quantity of acid. In other words, the presence of calcium sulphate compels the phosphoric

acid to do more work, and the final product is tricalcium instead of dicalcium phosphate.

This secondary reaction only takes place on heating, and is the more complete the longer the mixture is boiled. The practical effect of this in the use of tartar substitutes is of very great importance.

Goods of class I, whose neutralizing power depends entirely on their contents of monocalcium phosphate and free phosphoric acid, when mixed with sodium bicarbonate and water, liberate the carbonic acid gas at once and completely in the cold; and hence, if this combination is used in baking, it is necessary that the dough should be placed in the oven immediately after mixing, as otherwise the gas escapes and the resulting loaf is "heavy."

With goods of class II, on first mixing the dough a portion only of the gas is liberated (corresponding to the primary reaction), making the dough spongy, but on putting in the oven, the secondary reaction commences and a steady evolution of gas occurs, which keeps the loaf porous and light.

This two-fold reaction has, in fact, the same practical effect as is obtained by the use of a less readily soluble salt than monocalcium phosphate; *viz.*, the action is slower.

The special suitability of cream of tartar for baking powder purposes rests on its property of being only sparingly soluble in cold water, but quite readily so in hot water, the effect of which is that the carbon dioxide is developed in the right amounts at the right time; exactly the same result is obtained in tartar substitutes by means of the secondary reaction with calcium sulphate.

The calcium sulphate in some tartar substitutes cannot, therefore, be regarded as an adulterant, neither is it the result of carelessness on the part of the manufacturer; but it purposely forms part of the substance, and has an important, and for some uses, quite an essential function.

It is not my purpose at present to treat the matter from a hygienic point of view, but, inasmuch as calcium sulphate seems to be something of a bugbear to many health officers and state chemists, it may be pointed out that a greater part at any rate of this substance is actually converted in the baking process

into sodium sulphate, and further, that in the small amounts used in practical baking the resulting dose of the latter salt would be extremely small.

#### ANALYSIS OF TARTAR SUBSTITUTES AND STATEMENT OF RESULTS.

It might at first sight seem supererogatory to detail any methods of analysis of a material composed of such familiar substances as lime, phosphoric and sulphuric acids, magnesia, etc., etc., still more so to enter into a matter apparently so simple as the determination of the neutralizing power of an acid substance.

The determination of the working power of tartar substitutes, however, presents peculiar difficulties, so much so that an analyst inexperienced as regards these materials as a rule fails entirely to get results of any value whatever, and as regards the more complete analysis, the determinations of lime, phosphoric acid, etc., etc., indeed present no difficulty. But when the attempt is made to group the acids and bases, it frequently results in surprising misstatements.

A matter of primary importance in the analysis of tartar substitutes is the determination of the "strength," or neutralizing power, always stated in terms of sodium bicarbonate.

To determine this "strength," two obvious methods present themselves; *viz.*, titration with standard alkali, and the determination of the amount of carbon dioxide evolved from sodium bicarbonate by a known weight of the substance. Inasmuch, however, as the indications given by the above two processes are two entirely different things, it must first be decided before adopting one or the other method, exactly what is meant by "strength" in a powder of this kind.

When monocalcium phosphate and sodium bicarbonate are heated together in presence of water, the carbonate is decomposed until the salt  $\text{Na}_2\text{HPO}_4$  is formed. This salt, although chemically "acid," is already strongly alkaline to phenolphthalein, the salt of the formula  $\text{R}_2\text{H}_2\text{P}_2\text{O}_6$ , probably being the neutral salt to this indicator. It is obvious, therefore, that "acidity" of tartar substitutes, as indicated by titration, is quite a different matter from their ultimate power of determining the liberation of carbon dioxide from carbonates.

Ordinarily, for reasons above given, the "evolution" method indicates a power of evolving carbonic acid gas very considerably in excess of the "acidity" as indicated by titration. Unfortunately, however, both methods offer ample opportunity for error.

When a mixture of acid phosphate and sodium bicarbonate is heated with water, the amount of carbon dioxide evolved is dependent on the relative proportions of the two substances, on time, temperature, dilution and a host of other factors; and, by varying the conditions, results can be obtained differing from each other and the truth, not slightly, but to an extent to render the test useless.

In an article on the "Commercial Valuation of Cream of Tartar Substitutes," *J. Anal. Chem.*, 4, 4, Prof. Chas. A. Catlin sums up the foregoing in the words "there is found to be no definite ratio between the neutralizing capacity of these preparations and their gas-evolving power when in admixture with alkaline bicarbonate under the conditions of the baking process," and advocates the use of a modified form of the evolution method on the ground that inasmuch as the use of these powders is to evolve carbonic acid gas from alkaline bicarbonate, their power of doing this under the conditions of the baking process is the sole criterion of value.

There is, however, another factor that must be considered; *viz.*, the reaction of the residue. It is no less necessary that a baking powder shall have a neutral residue, than that it shall evolve carbonic acid gas, and there is this much in favor of the titration method, that if properly conducted it indicates exactly the amount of sodium bicarbonate that can be used with a given sample of tartar substitutes to give a neutral residue.

I can quite endorse Prof. Catlin's statement, that the ordinary method of titration with alkali, either direct or indirect, fails to give the proper data, but if the titration is conducted with special precautions, adapting it to the case, it is in my opinion the most satisfactory method of determining the "strength" of tartar substitutes.

The method of valuation proposed by Prof. Catlin is a combination of the titration and evolution methods; *viz.*, first find-

ing by titration with alkali and phenolphthalein the neutralizing power of the sample, and then weighing up exactly the amount of chemically pure bicarbonate, introducing into the evolution apparatus together with its equivalent of tartar substitutes, and weighing the carbon dioxide evolved under certain specified conditions.

It would seem that the evolution part of this method is entirely dependent on the titration, for certainly, if, in the evolution experiment only the exact equivalent of sodium bicarbonate as found by titration is used, the carbon dioxide corresponding to this and no more can possibly be evolved, and inasmuch as under the conditions laid down by Prof. Catlin for the evolution experiment, nearly all tartar substitutes will evolve carbon dioxide from more bicarbonate than is indicated by a properly conducted titration, the evolution experiment can at best only confirm the titration, and had better be altogether dispensed with as a troublesome and useless adjunct.

Prof. Catlin's paper contains many extremely valuable data as to the actual conditions to which the leavening agents are exposed in the practical baking process, and as emphasizing the necessity of making analytical tests as nearly as possibly under these conditions, is well worthy of attention.

The method of conducting the titration test differs with the character of the sample to be tested.

In the case of tartar substitutes of class I (*i. e.*, practically free from calcium sulphate) the amount of alkali neutralized is practically the same whether the titration be conducted hot or cold.

With class II, or intermediate grades containing any considerable amount of calcium sulphate, this is not the case, for when titrated in the cold, the solution reacts alkaline to phenolphthalein as soon as the primary reaction between soluble phosphoric acid and soda is complete. If now this solution be heated, the secondary reaction, previously explained, commences; the red color of the phenolphthalein gradually disappears, till on full boiling it will be found that a very considerable amount of alkali must be added before neutrality is restored. Hence, tartar substitute containing calcium sulphate shows one strength cold and a much greater strength hot; or, as it is expressed in trade, "sulphate of lime base goods show a *cold* test."

As before stated, in the case of goods free from calcium sulphate, the "hot" and "cold" tests are identical, or they "have no cold test."

It will be understood that the difference between the hot and cold test is purely a function of the secondary reaction with calcium sulphate, and from the relation between the two tests an expert can form a tolerably close estimate of the amount of this substance present.

To return to the titration, the test is best made on one gram of the substance suspended in about thirty cc. water in a porcelain basin, and titrating with caustic alkali (carefully freed from carbon dioxide), using phenolphthalein as indicator. The one essential of the method is to use a very large amount of the indicator. If the titration is made using only one or two drops of phenolphthalein, as would ordinarily suffice for an acidimetric titration, a far larger amount of alkali can be added, before the faintest pink color is obtained, than is really required. This may be readily shown by adding a further considerable amount of phenolphthalein when the faint pink darkens to deep red, and on titrating back with acid a considerable amount must be used before the color disappears. For this reason an inexperienced operator always obtains results far too high.

The most convenient method of procedure when working with unknown samples is, first to make a cold titration, adding a large amount of phenolphthalein and titrating to a faint pink. The alkali should be added drop by drop with constant and vigorous stirring to break up the little clots of precipitated phosphates formed by each drop.

In the case of sulphated goods the first pink tinge indicates the "cold test" and the burette reading should be recorded. The solution is then rapidly brought to a boil under the burette, and if the pink disappears more alkali is added till the very faintest color reappears.

This first test serves as a guide for a more exact titration in which it is best to add nearly the full amount of alkali required, drop by drop as before, then bring to a brisk boil, add the phenolphthalein and finish the titration rapidly while still actively boiling. The ending should be the first faint pink permanent

for one minute at a boiling temperature. The end reaction is not sharp and is very difficult to determine exactly.

With heavily sulphated goods prolonged boiling will cause the pink to disappear owing to the greater completeness of the secondary reaction; but as Prof. Catlin has pointed out, in the baking process the chemicals are exposed to a temperature of  $100^{\circ}$  for a period not exceeding one minute at the most, and therefore in the test this time of boiling should not be exceeded.

Any process of indirect titration, by adding alkali in excess and titrating back with acid is entirely inadmissible, as is also any separation of the insoluble portions of the powder by filtration before titrating.

The more complete analysis of a tartar substitute involves the determination of the phosphoric acid, and *the forms in which it exists*, the lime, magnesia, starch, sulphuric acid, and occasionally iron and alumina.

The determination of these substances requires no special notice, except as regards the forms in which the phosphoric acid exists, which is a matter of the highest importance in determining the relative merits of tartar substitutes.

Disregarding the small amounts combined with magnesia, iron, and alumina, the phosphoric acid in tartar substitutes is present in three different states:

“Free,” or uncombined.

Combined with one molecule of lime, as  $\text{CaH}_2\text{P}_2\text{O}_8$ .

Combined with more than one molecule of lime as insoluble phosphates; and in order to make an analysis of any value whatever, it is absolutely necessary to determine the amount present in each of these forms.

The “free” acid may be determined by titration with standard alkali and methyl orange, which indicator reacts neutral with salts of the formula  $\text{R}'\text{H}_2\text{PO}_4$ , and consequently indicates the “free” phosphoric acid only.

The titration is best effected on the filtered aqueous solution, adding standard alkali to pink-yellow color. Inasmuch as a slight precipitate forms before the point is reached the indications are a trifle too high, but sufficiently accurate for all technical purposes.

For the determination of the phosphoric acid existing as monocalcium phosphate and insoluble phosphates two analyses are necessary.

First, the *total* phosphoric acid on the solution of the powder in acid, and secondly, the "water soluble" phosphoric acid, best extracted by shaking a weighed quantity with water in a graduated flask, filtering clear and determining the dissolved phosphoric acid in an aliquot of the filtrate.

The phosphoric acid can of course be determined by any orthodox method, but for convenience and rapidity the volumetric method of Pemberton, (this JOURNAL, July, 1893) far surpasses any other.

The total phosphoric acid minus the "water soluble" gives the "insoluble" phosphoric acid, which may exist as  $\text{Ca}_3\text{P}_2\text{O}_8$ ,  $\text{Ca}_5\text{H}_2\text{P}_3\text{O}_{14}$ , or frequently as a mixture of the two. The determination of the insoluble phosphoric acid by difference is far more satisfactory than a direct determination.

The "water soluble" minus the "free" equals phosphoric acid existing as  $\text{CaH}_2\text{P}_2\text{O}_7$ .

It is necessary here to call attention to a very vicious practice followed by some chemists. Instead of determining the three forms of phosphoric acid as above, they determine only the *total* phosphoric acid and the total CaO. The CaO they then calculate into  $\text{Ca}_3\text{P}_2\text{O}_8$ , an excess of phosphoric acid of course remaining uncombined—which excess they then combine with the  $\text{Ca}_3\text{P}_2\text{O}_8$ , according to the reaction  $\text{Ca}_3\text{P}_2\text{O}_8 + 4\text{H}_2\text{PO}_4 = 3\text{CaH}_2\text{P}_2\text{O}_7$ , leaving an excess of either  $\text{Ca}_3\text{P}_2\text{O}_8$  or  $\text{H}_2\text{PO}_4$  as the case may be, but necessarily showing only one or the other.

Such a calculation cannot by any chance give correctly the composition of the substance for the reason before gone into, that tartar substitutes always contain both free acid and insoluble phosphates.

One word as to the form of stating results may not be out of place as this is a frequent source of *apparent* disagreement between two analyses that are really identical—a matter that it is often difficult to satisfactorily explain to the lay mind.

Having found, correctly or otherwise, the amount of monocalcium phosphate present in a sample, the analyst generally



states this in his report in the anhydrous form,  $\text{CaH}_4\text{P}_2\text{O}_8$ , calling it variously "monocalcium phosphate," "acid phosphate of lime," and occasionally "superphosphate," or some other name.

Equally in the case of calcium sulphate, it is a usual practice to report in the anhydrous form  $\text{CaSO}_4$ , and to call it variously "sulphate of lime," "gypsum," "terra alba," "plaster of Paris," etc., etc., according to the state of mind of the analyst. Even the starch present in tartar substitute is capable of being reported under the misleading term of "organic matter."

Having reported the salts as present in their anhydrous state, the difference between the sum of results and 100 is put down as "combined water," etc., etc.

While such a method of reporting is very convenient, as saving trouble of calculation and giving a pretty analysis adding up exactly to 100.00, it is doubtful if it is the best way.

In my opinion the results of an analysis should always be reported in a form as nearly approaching the truth as may be, and at any rate the statement should always show on the face of it exactly what is meant.

In the case in point, monocalcium phosphate always exists (and indeed can only exist) in a crystallized state, and in consequence it would seem to better represent the truth if stated in this form and called "crystallized monocalcium" or "acid phosphate."

With regard to the calcium sulphate in highly sulphated goods, it appears to exist partly in the anhydrous state and partly crystallized, and as it is impossible to determine the amount of water of crystallization, the exact statement of this cannot be made. It is, however, easy to convey exactly what is meant by stating either as "anhydrous" or "crystallized" calcium sulphate.

The practice of calling calcium sulphate found by analysis "terra alba," "gypsum," etc., etc., is to be unqualifiedly condemned, as it suggests, and is intended to suggest by implication, a fraudulent addition of a foreign substance,—a suggestion that is justified neither by the analytical data nor the real facts of the case.

The neutralizing strength should always be stated in terms of

sodium bicarbonate neutralized by 100 parts of the sample, and where there is a considerable difference between the hot and cold tests, this should be stated, as it is an important factor in deciding as to the suitability of a tartar substitute for any particular use.

The best grades in the market have a neutralizing strength of 100 parts equivalent to forty-four to forty-five sodium bicarbonate, *i. e.*, about the working strength of cream of tartar.

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[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE, No. 3.]

### THE ANALYSIS OF VARNISHES.

BY PARKER C. MCILHINEY, PH.B., A.M.

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**A**T present varnishes are seldom analyzed because no means are known of determining with any approach to accuracy, the amounts of the substances composing them. The tests used are practical ones and usually consist in varnishing a suitable surface with the sample to be tested and subjecting the varnished object to treatment as nearly as possible like that which it will receive in practice. If it is desired to ascertain the proportions of the different constituents, practical varnish-makers claim to be able to make up samples which will match in properties one to be tested, and in this way to arrive at the proper result. However this may be, it is out of the question for the chemist who is not a varnish-maker to use such a process. If methods can be devised whereby a chemist can make an actual analysis with a fair degree of accuracy, buyers can be certain of what they purchase and manufacturers can work more intelligently.

The different kinds of varnish may be classified as follows:

1. Spirit varnishes.
2. Volatile oil varnishes.
3. Fixed oil varnishes.
4. Miscellaneous; collodion varnishes, etc.

Spirit varnishes are composed of a resin dissolved in alcohol. Shellac spirits, made by dissolving shellac in wood or grain alcohol, is the most common.

Volatile oil varnishes are made by dissolving a resin in turpentine. Dammar varnish is a good example. Benzine is largely used as a substitute for turpentine in this and other varnishes.

The most important class is the fixed oil varnishes, and it is the analysis of this sort which will be considered. They are made from linseed-oil, a resin, and turpentine.

The principal resins used are kauri, manilla, and hard copals, such as Zanzibar. Common rosin is largely used as an adulterant. Kauri is the resin used by far the most, and there are many grades, varying in price from three cents to sixty cents a pound. Manilla stands next in the amount used, and of the others comparatively small quantities are used.

The resins used in fixed oil varnishes are in their natural state insoluble in linseed-oil and in turpentine. It is only after undergoing a process of roasting or distillation that they become soluble, and in this operation they lose from twenty to twenty-five per cent. in weight. In the process of manufacture the resin is first melted down in a kettle, and after it has been sufficiently heated the proper quantity of linseed-oil, also hot, is added, and the mixture heated some time longer to effect a combination between the oil and resin. After cooling somewhat, sufficient turpentine is added to properly thin the varnish.

It is difficult for several reasons to obtain samples of varnish for experiment in which the proportion of the constituents is known. They cannot be made successfully in small quantities as they are then of poor quality, and results obtained from such samples cannot be trusted. Through the kindness of Prof. A. H. Sabin, three samples of varnishes of known composition were obtained for experiment.

*The Determination of Turpentine.*—H. J. Phillips (*Chem. News*, **68**, 275, and *J. Soc. Chem. Ind.*, **10**, 577) proposes to distill off the turpentine at 220° C., using about 150 grams of varnish and catching the distillate in a tared flask. A current of coal-gas is passed through the liquid to prevent oxidation of the linseed-oil, and at the same time to assist in the removal of the turpentine vapor by carrying it away as fast as formed, and by agitating the liquid. The method is open to several objections; any vapors of naphtha in the coal-gas used are likely to be caught

and contaminate the turpentine. This difficulty would be overcome by the use of carbon dioxide instead of coal-gas, but carbon dioxide is not usually available in sufficient quantity. The author does not use any condenser, but depends upon the cooling of the neck of the retort used by the air, which is not sufficient. The residue left after most of the turpentine is gone is very viscous and retains some turpentine very persistently.

Mills (*J. Soc. Chem. Ind.*, 5, 222) says that the volatile constituents of varnish are easily determinable by evaporation with water.

Attempts were made to effect the removal of turpentine by distilling it off in a vacuum. Trials were first made using twenty-five grams of substance and a temperature of 100°–120° C., but this proved to be much too low a temperature and it was subsequently found that by using five grams instead of twenty-five grams of substance the results were better.

The method used was as follows: A portion of the varnish is weighed into a tared, round-bottom flask which is then heated in a paraffin bath at a temperature of 180° C. for four to eight hours, the air and vapor being removed from the interior of the flask by a pump. The flask is then again weighed and the loss in weight represents turpentine.

The results by this method were as follows:

Varnish used.	Per cent. of turpentine found.	Per cent. present.	Quantity of substance used.
A.....	52.7	60.0	25 grams.
B.....	34.9	41.4	25 "
C.....	52.7	56.9	5 "

The results are thus seen to be too low and irregular, and the residues smelled of turpentine. It was found that these traces of turpentine could be removed, and correct results obtained by adding to the contents of the flask after cooling two or three cc. of petroleum ether of very low boiling-point, allowing the residue to dissolve, and then carefully exhausting the flask of air, and finally heating gently. Of course, in these experiments it is necessary to use round-bottom flasks. The great objections to this method are that it does not distinguish between turpentine and any other volatile substance, and also that it requires arrangements for exhausting air, which are not always available. The

non-volatile residue is, however, in the very best condition for further examination.

Another method which has been used is a determination of the loss in weight on evaporating off the turpentine in the air-bath at  $100^{\circ}$  C. from a quantity of varnish contained in a watch-glass. This method is open to the same objections as the previous process, and the residue is not in good condition for further examination on account of the drying of linseed-oil. The fact that linseed-oil increases in weight on exposure to the air tends to give too low results. The formation of a film of dried varnish preventing further evaporation renders it necessary to use only small quantities of substance. In experimenting with the process it was found better to use watch-glasses of flat form than the ordinary concave ones. Three-quarters to one hour exposure at  $100^{\circ}$  and 0.400 to 0.500 gram substance gave the best results.

The following figures were obtained in this way:

Varnish.	Amount found.	Amount present.
B.....	40.8	41.4
C.....	56.0	56.9
D .....	53.4	56.8

The requirements of a satisfactory process for determining turpentine are:

(1) That the volatile material shall be separated under conditions which admit of its being actually weighed or measured and then submitted to further treatment.

(2) That the non-volatile portion shall be subjected to as little heat as possible, both to avoid any destructive distillation and to leave it unaltered for further examination.

(3) The process should require no unusual apparatus. None of these processes fulfill the above conditions.

It is well known that on distilling together two immiscible liquids, such as carbon disulphide and water, the boiling-point of the mixture is lower than that of the more volatile liquid. Carbon disulphide boils at  $49^{\circ}$ , but when distilled with water the boiling-point of the mixture is  $43^{\circ}$  (Kundt, *Jahresb. Fort. Chem.*, 1870, 49).

On distilling together 100 cc. of water and five cc. of turpentine it was found that the first ninety-five cc. of distillate contained all the turpentine which separated very well from the

water. Experiment showed that ninety cc. of water either dissolve or hold in suspension permanently about 0.3000 gram of turpentine. On these principles the following process was devised:

Twenty-five grams of varnish are weighed into a flask of 400 cc. capacity, in which has been placed a piece of granulated tin, or its equivalent, to prevent bumping and about ten cc. of water. The flask is in this way prevented from becoming greasy, which would cause violent bumping. The contents of the flask are now submitted to distillation, the distillate being caught in a tapped separator. When ninety or ninety-five cc. of water have come over, the distillation is stopped and the turpentine and water allowed to separate. If the contents of the flask still retain any odor of turpentine more water should be added and the distillation resumed. After settling for a sufficient length of time, the water is carefully drawn off and the turpentine poured into a tared flask and weighed. A correction is made for the amount of turpentine retained by the water, amounting to 0.300 gram for ninety cc. of water. In some experiments salt was added to the water to raise its boiling-point, but no apparent advantage was gained except when the non-volatile residue was heavier than water; in this case the salt prevented the residue from sinking to the bottom and causing bumping by greasing the flask. If it is desired to examine the residue, the remaining water is poured off from it and alcohol added. On distilling off the alcohol, and if necessary removing the last of it by the addition of a little ether, which is also evaporated off, the residue is obtained pure.

The following results were obtained by this process:

Varnish.	Per cent. found.	Per cent. present.
B.....	41.2	41.4
C.....	57.1	56.9
D.....	56.3	56.8

The sample D was made by dissolving common rosin in turpentine, and it was therefore more difficult to remove the last trace of turpentine from the non-volatile residue than it ever is in an oil varnish, but even in this case the result is fairly accurate.

The method requires no unusual apparatus and can be carried out in about half an hour. The residue is not heated above the

boiling-point of water, and the turpentine is actually weighed and may be itself analyzed.

For the determination of benzine in turpentine, the method of Burton (*Am. Chem. J.*, 12, 102) gives the best results. It depends upon the conversion of turpentine into acids soluble in water by the action of nitric acid while benzine remains unaffected and is separated and measured or weighed.

*The Non-volatile Portion.*—The analysis of the residue consisting of linseed-oil and resin, both more or less altered by heat, presents an extremely difficult problem in proximate analysis and one which yet remains unsolved.

The properties of resins have been investigated analytically by ;

Hirschsohn, *Pharm. Ztschr. f. Russland*, 1875, 225, and 1877, 1; *Pharm. Jour.*, 7, 369, and 8, 389.

Schmidt and Erban, *Sitz. d. Wiener. Akad.*, 94, 917, and *Ztschr. angew. Chem.*, 1889, 35.

Mills, *J. Soc. Chem. Ind.*, 5, 222.

Mills and Muter, *J. Soc. Chem. Ind.*, 4, 96.

Williams, *Chem. News*, 58, 224.

These investigators have made upon various resins the same tests which have been used in the analysis of oils; *viz.*, the acid figure, the Koettstorfer figure, the iodine figure, the per cent. of bromine absorbed, and the solubility in ether, alcohol, etc. Their results are given in the following table:

Resin.	Variety.	Acid figure.	Koettstorfer figure.	Per cent. Hölbl bromine figure. absorbed.	Observer.
Amber ...		15.4	86.8	62.1	Williams.
" ...		....	160.7	....	Mills.
" ...		....	145.0	....	Schmidt and Erban.
" ...		....	144.6	....	" " "
" ... Melted .....		0.0	38.9	4.8	" " "
" ... " .....		0.0	33.9	....	" " "
Animé.... Rough Demarara.....		26.6	73.6	127.88	Williams.
" .... Fine Zanzibar .....		18.2	73.6	135.25	"
" .... Unknown .....		25.2	87.5	137.54	
" ....		....	95.4	....	Mills.
Copal .... Soft manilla .....		131.6	184.1	137.79	Williams.
" .... Borneo manilla .....		141.4	176.7	138.04	"
" .... Singapore manilla .....		128.8	194.1	123.31	"
" .... Cleaned Sierra Leone ..		84.0	129.0	138.04	"
" .... Rough Sierra Leone....		72.8	138.5	133.35	"
" .... Rough Accra .....		46.2	131.6	121.66	"
" .... Rough White Cengola..		57.4	133.0	129.66	"
" .... Fine Clean Red Cengola		60.2	136.2	136.90	"

Resin.	Variety.	Acid figure.	Koett- storfer figure.	Hübl figure.	Per cent. bromine absorbed.	Observer.
Copal ....	Unknown .....	57.4	122.2	142.24	.....	Williams.
" .....	" .....	.....	123.9	.....	83.93	Mills.
" ....	Reduced to $\frac{1}{2}$ by boiling, ....	.....	128.9	.....	84.52	"
" ....	Boiled .....	114.4	.....	.....	.....	"
" ....	Zanzibar .....	.....	92.4	.....	.....	Schmidt and Erban.
" ....	" .....	.....	89.6	.....	.....	" " "
" ....	" melted .....	0.0	36.8	.....	.....	" " "
" ....	" .....	0.0	34.6	.....	.....	" " "
" ....	White Angola .....	.....	132.2	.....	.....	" " "
" ....	" .....	.....	129.7	.....	.....	" " "
" ....	" melted ..	93.6	118.8	44.9	.....	" " "
" ....	" ..	93.4	117.8	.....	.....	" " "
" ....	Red Angola.....	.....	148.0	.....	.....	"
" ....	" .....	.....	146.4	.....	.....	"
" ....	" melted .....	30.5	110.7	34.8	.....	"
" ....	" .....	30.0	109.8	.....	.....	"
Dammar, Batavia .....	.....	22.4	36.4	117.67	.....	Williams.
" .....	Unknown .....	26.6	31.1	142.24	.....	"
" .....	" .....	.....	52.3	.....	117.94	Mills.
" .....	" .....	33.0	47.1	63.6	.....	Schmidt and Erban.
" .....	" .....	30.6	46.5	63.5	.....	" " "
Elemi ....	" .....	15.7	28.6	175.39	.....	Williams.
" .....	" .....	.....	32.9	.....	122.23	Mills.
" .....	" .....	22.3	25.1	85.1	.....	Schmidt and Erban.
" .....	" .....	22.0	24.0	80.9	.....	" " "
Kauri ....	Medium.....	63.0	99.3	151.13	.....	Williams.
" ....	Fine .....	51.8	77.4	164.21	.....	"
" .....	" .....	.....	128.8	.....	108.22	Mills.
Rosin.....	Refined .....	179.2	187.4	115.31	.....	Williams.
" ....	" .....	177.8	195.7	114.80	.....	"
" ....	Ordinary.....	169.4	176.4	112.02	.....	"
" ....	" .....	166.6	190.1	132.28	.....	"
" ....	Refined .....	.....	181.0	.....	112.7	Mills.
" ....	Average of 5 samples ..	.....	.....	155.5	.....	McIlhiney.
" ....	Window glass .....	159.1	170.4	.....	.....	"
" ....	E. ....	168.5	189.9	.....	.....	"
" ....	A. Black.....	155.7	195.1	.....	.....	"
" ....	" .....	146.5	168.2	116.8	.....	Schmidt and Erban.
" ....	" .....	145.5	166.0	114.6	.....	" " "

The corresponding figures for linseed-oil are as follows:

Acidity should be 0.0. Mills allows one per cent. KOH for acidity.

Koettstorfer figure (Allen, *Commercial Organic Analysis*, 2, 42). Nine samples, 187.4-195.2.

Hübl figure (Allen, *loc. cit.*, 50). Raw oil, 155-160; boiled oil, 148. Holde, *Mittheil. K. tech. Vers. Berlin*, 1891, 9, 81, and *J. Soc. Chem. Ind.*, 12, 179-180, 954.

Bromine absorption (Levallois, *J. pharm. chim.*, 1887, 1, 334), 100 per cent.



Mills (*J. Soc. Chem. Ind.*, 2, 436). Raw oil, 76.09 per cent. ; boiled oil, 102.36 per cent.

McArthur (*J. Soc. Chem. Ind.*, 7, 64). Raw oil, 65.0-65.3 per cent. ; boiled oil, 63.2-66.3 per cent.

The differences in solubility between linseed-oil and melted resins are but slight and are of little value in effecting separations in varnish analysis.

The Hübl figure is evidently useless as a means of quantitative analysis for the figures of linseed-oil and kauri the most frequently occurring resin, are almost identical.

The difference between the Koettstorfer figure is only about seventy-five, and even supposing that the figures of both oil and resin are known accurately, which is not the case, it would be difficult to make the analysis so carefully that the percentages of oil and resin would be correct.

Mills states that the analysis may be made by determining the acidity to phenolphthalein, and this proved to be correct, provided the mixture is composed of common rosin and linseed-oil and is not heated long. An analysis of such a mixture gave correct results but on attempting to apply the process to properly made varnishes the process was unsuccessful. Ten grams of a sample of varnish, known to contain 14.36 per cent. of kauri-resin, were diluted with a mixture of absolute alcohol, ether, and petroleum ether to obtain a clear solution, and then titrated with a solution of caustic soda in alcohol using phenolphthalein as indicator. The acidity found in this way was equal to only 0.345 per cent. of potassium hydroxide; this would mean an acidity of 2.40 per cent. for the kauri present, whereas Mills found 11.44 per cent., and Williams 6.3 per cent. Mills' statement that "it is evident that boiled oil when heated with a resin makes no difference in the resin's acidity," is not sustained by the facts.

The amount of bromine absorbed, as determined by the methods of Allen, Mills, and Levallois, is of no more use than the Hübl figure. The results depend largely upon the conditions under which the analysis is conducted.

In view of the fact that the bromine-addition figure of rosin is 0.0, while that of linseed-oil is 102, it seemed very likely that by means of this figure it would be possible to analyze varnish

residues. To test the process, a mixture was made of fifty per cent. common rosin and fifty per cent. oleic acid. The bromine-addition figure of the oleic acid used was 51.78 per cent., and that of the mixture 25.7 per cent., corresponding to 49.6 per cent. of oleic acid instead of fifty per cent. In order, if possible, to obtain samples of boiled oil and kauri-resin in the same condition in which they are present in varnishes, a quantity of boiled oil was heated in a retort to a temperature of 290° C. and maintained at this temperature for one hour. A sample of clear kauri-resin was also heated in a retort until it had lost twenty-three per cent. of its weight. The non-volatile part of a varnish of known composition was analyzed at the same time. The figures obtained were as follows:

Substance.	Bromine-addition figure.	Bromine-substitution figure.
Heated linseed-oil .....	76.62	4.82
Melted kauri-resin.....	21.53	80.31
Non-volatile of varnish C.....	89.16	22.84
Kauri, 54.3 per cent., oil, 45.7 per cent. }		
Theoretical figures of above.....	46.71	45.81

The process therefore fails to give any means of making this analysis on account of changes made by the process of manufacture in the properties of oil and resin. It is well known to varnish-makers that treating together, effects remarkable changes in their physical properties, and that a certain amount of heating is necessary to make them knit together and work properly in the finished varnish.

Gladding (*Am. Chem. J.*, 3, 416), has devised a process for determining common rosin in mixtures with fatty oils, depending upon the solubility of silver resinate in ether and the insolubility of silver oleate in the same medium. This process was tried on varnish but also failed to give satisfactory results. A varnish known to contain 14.36 per cent. of Kauri resin gave 25.9 per cent.

It is evident that the processes used in oil analysis are not adapted to the analysis of varnishes. The oil and resin react upon each other in some way not understood, giving rise to new compounds, and we must know something about what these compounds are, before the analytical problem can be solved.

## THE ANALYSIS OF MALT.

BY JOHN A. MILLER, PH.D.

Received March 19, 1894.

HAVING been called upon during the past few years to assay a great many samples of malt I have been struck by the variation which existed between the results of my own analyses and those made by other chemists upon the same samples. The variations in some cases were too large to be placed within the possibility of experimental error. With the belief that these variations might, in part at least, be due to a greater or lesser degree of accuracy in the methods employed in the analysis of malt, I undertook a comparative investigation of three methods which are quite universally used.

From the stand-point of the brewer, the largest consumer of malt, what are the important points to be ascertained by the analysis of a malt sample?

1. Moisture.
2. Percentage of extract which the malt will yield when submitted to a miniature mashing process.
3. Diastatic power, that is the rapidity with which the starch contained in the malt is converted into sugar and dextrine.
4. The percentage of acidity (calculated as lactic acid) which the wort contains.

It has been claimed by some that the percentage of sugar formed and the amount of proteids dissolved is of importance in judging of the character of the malt. The amount of sugar is of no practical value to the brewer as the increase or decrease of the percentage of that article is entirely dependent upon the manner in which the malt is handled in the mash tub. The total nitrogen in the malt wort calculated as proteids is of little value since the percentage present in the finished beer will depend upon so many factors as to render the first results of comparatively little value. Amongst the factors which will influence this percentage are: Character of the water used in mashing; the use of a high or low initial mashing temperature; the length of time the wort is boiled in the kettle; the amount and character of the hops used; the character and quantity of yeast used; and the character of the fermentation.

The four points mentioned are of about equal importance in the assay of a malt sample.

The determination of moisture shows whether the malt has been properly dried and also whether the purchaser is not paying too high a price for an article which he can obtain very readily from the city water supply.

The determination of lactic acid is of value from the fact that it enables one to judge, within reasonable limits, of the age of the malt under examination. For example, a sample of malt which is low in moisture and high in lactic acid is an old malt which has been redried to bring down the high percentage of absorbed moisture.

In a first-class sample of malt the moisture should not run above five per cent., and the lactic acid 0.7 per cent.

*Determination of Moisture.*—Two methods were investigated in order to ascertain their relative accuracy. In the one method from two to four grams of ground malt was used; in the other twenty grams. In both cases the samples were heated to 100° C. until the weight was constant. Both methods gave results agreeing to within the third decimal place. The use of from two to four grams, however, is to be recommended:

1. Because it admits of the use of ground watch crystals for drying and weighing, thus preventing the absorption of moisture while the sample is cooling.

2. The time required to obtain a constant weight is much less than when twenty grams are used.

*Determination of Extract.*—The determination of the percentage of extract which a malt will yield is of very great importance, as upon this percentage, the value of the malt largely depends. It is evident that a sample of malt yielding fifty-five per cent. of extract has not the same commercial value as a malt yielding sixty per cent.

#### METHOD NO. I.

“Fifty grams of ground malt are weighed out as rapidly as possible (to avoid accession of water) and treated in a weighed beaker with 250 cc. of warm distilled water, of such a temperature that the initial heat of the mixture may be from 50°–52° C. The beaker containing the mash is placed in a water-bath and

the contents maintained at the same temperature for a quarter of an hour. The heat is then gradually raised till the immersed thermometer registers  $59^{\circ}$ – $60^{\circ}$  C., and the temperature is then kept constant till a drop taken from the liquid ceases to give a blue color with iodine solution and nearly ceased to give a brown. This shows that all the starch and nearly all the erythrodextrine has suffered hydrolysis—a point which will be reached in about twenty minutes. The heat is then increased to about  $70^{\circ}$  C. in order to complete the saccharification, when the water in the bath is boiled for five minutes. This step which completes the process of mashing should be arrived at in about 100 minutes from the commencement of the operation. The beaker is then cooled and the contents filtered. The insoluble matter is washed with cold water and the filtrate is made up exactly to 400 cc. The density of the clear wort is next taken at  $15.5^{\circ}$  C. in the usual way by a specific gravity bottle. The excess of density over that of water (taken as 1,000) multiplied by 2.078 will give the percentage of dry extract yield by the malt. Instead of ascertaining the gravity of the infusion, the proportion of solid matter may be determined by evaporating a known measure of the wort to dryness in a flat-bottomed dish, so that the residue may form a thin film. The extract dried at  $105^{\circ}$  C. till constant in weight."

Two portions of fifty grams each of the same sample of malt treated as indicated above gave the following results:

	I.	II.
Specific gravity of the wort....	1.0284	1.0284
Extract calculated by factor....	59.01 per cent.	59.01 per cent.

5.142 grams of the wort were then taken and placed in a wide flat-bottomed platinum dish and the extract dried at  $105^{\circ}$  C. to almost constant weight. The following was obtained:

	I.	II.
Weight of the extract .....	0.3496 gram.	0.3488 gram.
Average weight .....	0.3492 gram.	
Percentage of extract.....	55.87	

5.142 grams were again taken and placed in a flat-bottomed dish and this in a water oven, the temperature of which was kept at  $70^{\circ}$ – $75^{\circ}$  C., and the extract dried to constant weight. The time required for this was about seventy hours.

	I.	II.
Weight of the extract .....	0.3694 gram.	0.3681 gram.
Average weight .....	0.3687 gram.	
Percentage of extract.....	58.992	

## METHOD NO. II.

"Fifty grams of ground malt are carefully weighed as rapidly as possible. The ground malt is put into a copper beaker, the weight of which is known, and this beaker is placed in a water-bath. Water is now mixed with the malt to the amount of 200 cc., at a temperature of 38° R. This temperature is held while the malt is continuously stirred for thirty minutes, when the temperature is raised to 58° R., 4° R. each five minutes. When the temperature of 58° R. is reached tests are made in order to find out whether the starch has been converted completely. Usually we find that after the temperature of 58° R. has been reached all the starch is converted. The mash is always held thirty minutes after the temperature of 58° R. has been reached, when it is boiled for five minutes, cooled off, and water enough is added to make the weight of the contents of the beaker, or the weight of the entire mash, 350 grams. The wort is then filtered off. After the wort has been filtered the specific gravity is taken from which the per cent. Balling is ascertained and the amount of extract in the malt computed to the following formula; *viz.*,"

$$\frac{(600 + \text{per cent. water}) \times \text{per cent. Balling}}{100 - \text{per cent. Balling.}}$$

Two mashes of fifty grams of malt gave the following:

	I.	II.
Specific gravity of the wort .....	1.0385	1.0383
Average specific gravity .....	1.0384	
Extract calculated by formula.....	63.85 per cent.	
Moisture in the malt .....	7.53 " "	

5.192 grams of wort was then placed in a flat-bottomed dish and dried at 105° C. to almost constant weight. Results; *viz.*,

	I.	II.
Weight of extract.....	0.4520 gram.	0.4522 gram.
Average weight .....	0.4521 gram.	
Extract .....	54.25 per cent.	

The same amount of wort dried at 70°-75° C. for about seventy hours gave:

	I.	II.
Weight of extract .....	0.4924	0.4922
Average weight .....	0.4923 gram.	
Extract .....	59.07	per cent.

## METHOD NO. III.

Fifty grams of ground malt are weighed out as rapidly as possible, then placed in a weighed copper beaker and mixed with 200 cc. of water of a temperature of 40° C. The whole mixture is then carefully heated on an asbestos plate until the immersed thermometer registers 60° C. This temperature of 60° C. is maintained for twenty minutes, the mixture being almost constantly stirred during this time. At the end of twenty minutes a few drops of the solution are tested with iodine solution in order to ascertain whether the saccharification is complete. If the iodine gives the starch or erythrodextrine reaction the mash is further heated, the temperature being carefully raised 1° every two minutes until iodine solution ceases to give any reaction. It is very seldom that the temperature will go above 70° C. The flame is then removed, the mash cooled down and enough water added to make the total amount used equal to 400 grams, or the weight of the mash, that is, the malt plus the water equal 450 grams. After thoroughly mixing, the mash is thrown upon a plaited filter. The first half of the wort which filters through is thrown back upon the filter and then all which filters through collected. The specific gravity of this filtrate, or wort, is then taken by means of the Westphal balance. From this gravity the percentage given by Schultze's tables is ascertained and that number multiplied by 8.75, which gives the percentage of dry extract yield from the malt. The percentage can also be calculated by the use of the following formula:

$$\frac{(800 - \text{per cent. water}) \times \text{per cent. Schultze}}{100 - \text{per cent. Schultze.}}$$

The Schultze tables are so arranged that they give the amount of extract in 100 grams of wort of the specific gravity obtained. It would be a natural conclusion that the percentage represented by Schultze tables should be multiplied by 8 in order to obtain the amount of extract in 100 grams of malt, but this factor gives results which are below the absolute amount of extract which may be obtained from the malt. As the result of actual

brewing experience I am of the opinion that the percentage Schultze multiplied by the factor 8 represents the amount of extract which the average brewer obtains from his material in actual practice, although the absolute amount obtainable on a small scale is higher. Two mashes of fifty grams each gave:

	I.	II.
Specific gravity of wort.....	1.0285	1.0285
Extract calculated from Schultze's table. Factor 8.....	58.96 per cent.	58.96 per cent.
Factor 8.75.....		
Extract calculated by formula.....	64.24 " "	64.24 " "

5.1425 grams of this wort were placed in a flat-bottomed dish and dried at 105° C. to almost constant weight. Results; *viz.*,

	I.	II.
Weight of extract.....	0.3511 gram.	0.3494 gram.
Average weight of extract.....	0.3502 gram.	
Extract.....	56.03	per cent.

The same amount dried at 70°-75° C. for about seventy hours to constant weight gave:

	I.	II.
Weight of extract.....	0.3700 gram.	0.3681 gram.
Average weight .....	0.3690 gram.	
Extract.....	59.04	per cent.

In order to ascertain what variation, if any, existed between these results and the absolute amount of extract obtainable I made another mash from the same sample of malt which had been used for the preceding experiments. Method No. III was used with this exception that it was not made up to 400 grams, but was at once thrown upon a filter and washed with water at a temperature of 58° C. until the filtrate gave no reaction for sugar with Fehling's solution. This filtrate was then made up to 1,000 cc. and an aliquot part dried at 70°-75° C. to constant weight. Two portions of ten cc. each gave:

	I.	II.
Extract by weight in ten cc....	0.3237 gram.	0.3236 gram.
" in 1,000 cc.....	32.37 " "	32.36 "
Percentage of extract from malt, 64.74		64.72
Average percentage .....		64.73.

The variations existing between the results obtained is apparent in the following table:



	No. I.	METHODS.	
		No. II.	No. III.
Per cent. of extract calculated according to the directions of the method,	59.01	63.85	64.487
Method III using factor 8.....	....	....	58.96
"    "    "    formula.....	....	....	64.24
Extract dried at 105° C. ....	55.87	54.25	56.03
"    "    "    70°-75° C. ....	58.99	59.07	59.04
Absolute per cent. of extract obtainable, ....	....	....	64.73

A comparison of these results show that methods II and III give us figures agreeing closer to the actual amount of extract obtainable from the malt than method No. I, but even these are a little below the actual content. No. III, however, only slightly so. The results obtained by drying at 105° C. are too low and untrustworthy owing to a decomposition during the process of drying, as will be shown later in this paper. Looking at the results of the three methods as obtained by drying the extract at 70°-75° we find an excellent agreement between the maximum and minimum results, but a wide variation from the absolute amount of extract. This would indicate that a marked amount of starch was not saccharified and consequently would be lost as extract. It was only obtained by the washing of the grains with warm water.

*Extract dried at 105° C.*—In order to ascertain why the extract dried at 105° C. was so much lower than when calculated or dried at 70°-75°, a malt analysis was made with the following results:

	Method III.		
Calculated per cent. of extract using factor 8,	58.40	per cent.	
Extract dried at 70°-75° .....	58.25	"	"
"    "    "    105° .....	54.01	"	"

The percentage of extract obtained by drying at 105° is over four per cent. lower than the percentage of extract obtained by the other methods. This would indicate that either the percentage of extract was actually lower than indicated by the other methods of determination, or that some substance had undergone decomposition and occasioned a loss which reduced the percentage. I was of the belief that the maltose had suffered decomposition at the temperature of 105° and therefore lowered the percentage of extract.

Determinations of sugar were consequently made:

1. In the wort obtained by method III and calculated to the total amount of extract obtained.

2. The maltose or sugar contained in the extract dried at  $70^{\circ}$ – $75^{\circ}$  was determined and a calculation made for the total from these results.

3. The sugar contained in the extract dried at  $105^{\circ}$  was determined and a similar calculation made.

	Maltose.
Method No. III .....	37.50 per cent.
Extract dried at $70^{\circ}$ – $75^{\circ}$ .....	37.50 " "
" " " $105^{\circ}$ .....	31.50 " "

It will be seen that the percentage of maltose obtained from the extract dried at  $105^{\circ}$  is six per cent. lower than that obtained from the original wort and from the extract dried at  $70^{\circ}$ – $75^{\circ}$ . This rather clearly indicates that a decomposition of maltose has taken place with a consequent loss.

In every case the extract dried at  $105^{\circ}$  was almost black in appearance and had a distinct burnt sugar odor.

#### CONCLUSIONS.

1. Methods II and III give results almost equal in accuracy. No. III giving nearer the absolute amount of extract obtainable when the factor 8.75 is used. It is furthermore a preferable method as it requires less time for the analysis than No. II. And where a number of samples are handled, time is an important item.

2. Method I is inaccurate as the results obtained are much below the actual amount of extract.

3. The extract can not be determined by drying at  $105^{\circ}$  owing to the decomposition of the maltose at that temperature. This applies to the determination of extract in beer as well as in unfermented worts.

4. The washing of the grains until no sugar reaction is obtained and the subsequent drying of the extract at  $70^{\circ}$ – $75^{\circ}$  C. is impracticable, except for scientific purposes, as the amount of time required for the completion of an analysis is too great.

I would recommend method III as the simplest; it is accurate when the factor 8.75 is used, and requires the least time. It is the method upon which a subsequent paper on diastatic power will be based.

I wish, here, to express my sincere thanks to my assistant, Mr. W. I. Tibbals, for the very able and enthusiastic manner in which he has assisted me in this investigation.

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### THE IODIDES OF NARCEINE.

BY G. B. FRANKFORTER.

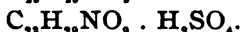
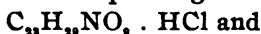
Received April 16, 1894.

THE alkaloid narceine when treated with iodine forms a characteristic blue substance analogous in many respects to the blue substance formed by the action of iodine on starch. This blue substance was first observed by Stein<sup>1</sup> in the early history of the alkaloid who regarded it as a periodide of narceine; but as pure narceine was then unknown, and as no definite formula was given for the substance, due allowance must be made in accepting his work.

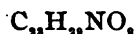
The isolation of pure narceine and the determination of the new empirical formula, as well as the synthetic structure,<sup>2</sup> has made it necessary to repeat all of the early investigations. So far, at present, as this repetition has been carried out, different conclusions have been reached. This fact explains in a degree the variations and contradictions of the early investigators. The formula of narceine was finally fixed by Anderson<sup>3</sup> as



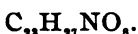
and salts were prepared corresponding to



Later work on the alkaloids shows that both the chloride and sulphates are not salts of the base



but of a base containing one molecule of water less,



<sup>1</sup> Fresenius' *Zeitschrift für analytische Chemie*, 9, 390.

<sup>2</sup> Frankforter, "Beitrag zur Kenntniss des Narceins." Inaug. Dis., Berlin.

<sup>3</sup> Anderson, *Liebig's Annalen d. Chemie. and Pharmacie.*, 86, 182.

In like manner the iodides of narceine were found to be derivatives, not of the Anderson formula, but the same less one molecule of water.

*The Blue Iodide.*  $((C_{27}H_{27}NO_3)_2I_2 + 3H_2O)$  When narceine is treated with a water solution of iodine the blue iodide is formed, varying in color from a gray to an indigo blue, according to the amount of iodine used. By treating crystals of narceine direct with iodine, indigo-blue crystals are formed which still retain the same crystal form of narceine. By heating they change from long fine prismatic needles to short irregular ones. The blue crystals are slightly soluble in water, soluble with difficulty in alcohol, and quite insoluble in ether and chloroform.

On treating with dilute sodium hydroxide the blue color disappears, and when excess is avoided fine felt-like crystals of narceine are formed. By treating the blue crystals suspended in water with silver nitrate in the presence of nitric acid, beautiful hexagonal columns are formed which are now in process of analysis. The blue crystals contain three molecules of water which may be removed at  $100^\circ C$ .

0.3836 gram of the iodide lost 0.0118 gram at  $100^\circ$ .

Found, $3H_2O$ .	Calculated for, $(C_{27}H_{27}NO_3)_2I_2 + 3H_2O$ .
3.07 per cent.	3.29 per cent.

#### ANALYSES:

- I. 0.2020 gram iodide gave 0.4050 gram  $CO_2$ , 0.1107 gram  $H_2O$ .  
 II. 0.2632 " " " 0.5294 " " 0.1424 " "  
 III. 0.3109 " " " 0.0912 " AgI.

I.	Found, II.	III.	Calculated for, $(C_{27}H_{27}NO_3)_2I_2$ .
C 54.65 per cent.	54.82 per cent.		54.63 per cent.
H 6.08 " "	6.00 " "		5.10 " "
I		15.95 per cent.	16.01 " "

Dried at  $120^\circ$ – $130^\circ$  the blue color changes to a brownish, but changes back to the blue on cooling. The dried substance melts at  $176^\circ$ – $177^\circ C$ . If heated rapidly a melting point of  $180^\circ$ – $181^\circ$  may be obtained.

*The Red Iodide.*  $(C_{27}H_{27}NO_3)_2I_2$ . It was found that by treating narceine with an alcoholic solution of iodine a grayish-blue substance was formed which proved to have different properties

from the blue iodide. On standing in the air, or by gently heating, it changes to a red color and loses its well-defined crystal form. Dried at  $110^{\circ}$ – $120^{\circ}$  it becomes brick red and changes slightly to the blue on standing some days in the air. It melts at  $181^{\circ}$  and is insoluble in water, alcohol, and ether. It contains three molecules of water which may be removed by drying at  $90^{\circ}$ – $100^{\circ}$ .

0.2209 gram iodide dried at  $100^{\circ}$ – $110^{\circ}$  lost 0.0092  $\text{H}_2\text{O}$ .

Found,  $3\text{H}_2\text{O}$ .  
4.12 per cent.

Calculated for,  
 $(\text{C}_{22}\text{H}_{27}\text{NO}_8)_2\text{I} + 3\text{H}_2\text{O}$ .  
3.56 per cent.

Analyses gave numbers which correspond best to the above formula.

#### ANALYSES:

I. 0.1826 gram iodide gave 0.3770 gram  $\text{CO}_2$ , 0.1025 gram  $\text{H}_2\text{O}$ .  
II. 0.3763 " " " 0.0546 " AgI.

	I	Found,	II
C	56.35	per cent.	
H	6.23	" "	
I			7.84 per cent.

	Calculated for, $(\text{C}_{22}\text{H}_{27}\text{NO}_8)_2\text{I}$ .
	56.63 per cent.
	5.54 " "
	8.00 " "

Like the blue iodide it is transformed into narceine by carefully neutralizing with sodium hydroxide. In the presence of an alkali no iodide is formed. By treating with silver nitrate, slightly acidulated with nitric acid, fine long hexagonal columns crystallize out, on standing some hours in a cool place. The crystals are soluble in water and alcohol and melt at  $110^{\circ}$ – $112^{\circ}$ . They are in process of analysis. It will be observed that the analyses give the per cent. of hydrogen too high. This was also observed in a great many analyses made in determining the new formula for narceine. In all these analyses, some of which were made by professional analysts, the hydrogen ran too high. So that it is barely possible that the formula for narceine may be changed from  $\text{C}_{22}\text{H}_{27}\text{NO}_8$  to  $\text{C}_{22}\text{H}_{28}\text{NO}_8$ . This would raise the per cent. of hydrogen to 6.24, while the average of ten analyses made by four analysts gave an average of 6.4 per cent. This work was begun in the University of Nebraska, and for many favors received there, I wish to thank Prof. H. H. Nicholson.

## SOME SOURCES OF ERROR IN OUR METHODS OF DETERMINING POTASH IN FERTILIZERS AND GERMAN POTASH SALTS.<sup>1</sup>

BY N. ROBINSON, REPORTER ON POTASH FOR THE N. A. O. A. C. FOR 1893.

I N common with many others, the writer has for some time entertained the belief that none of our recognized or official methods for determining potash in fertilizers and potash salts were above criticism. The objections to our American official methods from German and other sources are entitled to the highest respect, and per contra, the grave doubts expressed in high quarters among chemists in this country, as to the validity of the superior claims made for the Anhalt or Stassfurt methods, determined the writer for his own satisfaction to undertake a series of experiments, to ascertain, if possible, the sources of error, if any should be found to exist, in the three best known and most widely used ways of potash determination; viz., the official or Lindo-Gladding, the alternate, and the Stassfurt or Anhalt methods.

This series of experiments was begun over two years since, and has been prosecuted as time permitted from that period to the present. The writer is constrained to admit that he had at the beginning a very inadequate conception of the difficulties to be encountered in the solution of the problem, or the wide scope of inquiry which anything like an exhaustive study of the question involved.

The literature of the matter, while sufficiently voluminous on the general subject of potash determination, seemed to stop short at the very point where these inquiries must begin. Teschemacher and Smith, with the sanction of Fresenius and the apparent acquiescence of all the best German authorities, had declared that the removal of sulphuric acid was a *sine qua non* in all accurate potash estimations which, of course, at once excluded our chief American method from the list of "accurate" ones. Then came Zimmerman with a general and certainly rather formidable indictment of this same method. He charged that the

<sup>1</sup> Read before the World's Congress of Chemists, August 22, 1893.

ammonium-chloride solution was far from being a harmless and indifferent solvent of the miscellaneous impurities which are usually found in the potassium-platinochloride precipitate as obtained by the Lindo-Gladding method. Exact details were, however, wanting, or, at least not obtainable in any publication within the reach of the writer. Since then it is understood that one or two chemists in this country have undertaken investigations similar to those made by the writer, albeit the results of their work, perhaps from his somewhat isolated position, have failed to reach him.

It is with no little hesitancy, and he trusts with becoming modesty, that he is compelled to come into court with a general indictment against all our recognized or official methods of determining potash in fertilizers and potash salts. The writer does not make this sweeping charge lightly or without a full estimate of its gravity and of the overwhelming weight of authority which is likely at once to be marshalled against it. Methods of recognized value and almost universal acceptance are not dislodged without a struggle. The writer can only plead the evidence of the facts which he gives, and look patiently to the "calm judgment of the coming time" for the vindication of views which are presumably too radical for general acceptance, except as the result of extended and patient research at the hands of abler investigators than himself.

*The First Count Against All Three Methods.*—The first count in the indictment, and which is common to all our methods, comes from an obscure phenomenon, which so far as I am aware, has never been thoroughly investigated. For want of a better name I shall call it "The occlusion of potash salts by precipitates." Certain precipitates have long been known to manifest this peculiarity; but the bearing of this upon potash estimation seems somehow to have been overlooked. The fundamental fact is this. Many precipitates carry down potash salts and hold them so tenaciously that they cannot be washed out with hot water. All the precipitates thrown down in the customary working of our various official methods manifest more or less of this same tendency. Barium sulphate is probably the worst offender. Ferric and aluminic compounds are scarcely less chargeable with

this occult species of chemical larceny, while calcium, magnesium, and the other salts of the alkali metals are by no means free from suspicion of at least a mild form of the same tendency to hide and hold potash.

*The Lindo-Gladding Method.*—According to the investigations of Zimmerman and others—investigations which the tabular estimates by the writer given below, seem to fully confirm, in addition to the above source of loss coming from the “occlusion” of potash in “precipitates,” there are two other distinct and constant sources of error, with a number of casual and incidental ones, which may additionally vitiate results.

The first comes from the “alcohol washings” which, in the presence of the miscellaneous impurities nearly always found in the potassium platinochloride precipitate obtained by this method, result in the solution and consequent loss of the latter; and the second, from the fact that the solvent action of ammonium-chloride solution does not stop with the foreign salts which it is designed to remove; but that double decomposition often takes place. Potash is removed and ammonia substituted, involving the weighing of an impure potassium platinochloride, a portion of which is of different molecular weight. If we add to this the fact that calcium and magnesium sulphate, as well as ammonia, are not infrequently present in this same platinochloride, even when “washed to constant weight,” we are certainly entitled to suspect the absolute correctness of all potash estimates made by the Lindo-Gladding method.

Before giving tabulated results the writer may be pardoned for outlining in the briefest manner, the methods used in the work. In all cases, precipitates were washed with hot water until some time after any cloudiness was perceptible in the filtrate, either with barium chloride or silver nitrate. Potash was recovered from precipitates thrown down by ammonia and ammonium oxalate by re-solution and reprecipitation, and from barium sulphate by boiling the filter and its contents twice in dilute hydrochloric acid. The recovery of the potash from the ammonium-chloride washings seems to present the greatest practical difficulty. The ordinary method of volatilizing the ammonium salts over an open Bunsen flame involved so much loss of potash that no reliance



could be placed on the results. Fair work was done by exposing the well-dried material in a thin layer, in a shallow flat-bottomed platinum capsule on a portion of the sand-bath where the heat could be kept at the lowest vaporizing temperature of ammonium chloride, and consuming five or six hours in the operation. Another method involving several evaporations, incinerations, and filtrations with a slight loss of potash, was to add to the washings enough sulphuric acid to change all bases into sulphates, with appropriate subsequent treatment. The recovery of the potash from the "alcohol washings" seemed to present no special difficulty.

A word as to the factor of correction used for the potash already present in the ammonium-chloride solution. In my first experiments I assumed that the amount of potash present could be correctly estimated "by difference," by simply subtracting the weight of the undissolved portion from the five grams of potassium platinochloride first placed in the 500 cc. of the washing-fluid. The factor, 0.000195 per cc. thus obtained was used until recently without a suspicion of its inaccuracy. Some inexplicably discordant results led to a careful review of the whole matter. Analytical determinations showed that nearly twice as much potash was present in my ammonium-chloride solution as I had supposed. On carefully carrying out the official directions with another lot of this ammonium-chloride solution, I found that the potassium platinochloride had done something else besides "settle over night." Mutual decomposition had taken place. The ammonium-chloride solution was found to contain about as much potash in the form of chloride as platinochloride. The undissolved portion was a mixture of potassium platinochloride and ammonium platinochloride. The final amount as ascertained by several analytical determinations of the solution actually used, was potash corresponding to 0.00039 potassium platinochloride to the cubic centimeter, and the work as now given is corrected by that factor.

Still another factor of correction, small in all probability but still necessary for exact work, may be casually referred to. It is more than doubtful whether the potassium platinochloride precipitate obtained by the Lindo-Gladding method—in spite of all

its numerous "washings"—is ever strictly chemically pure. My observations indicate that, in addition to ammonium platinochloride, calcium and magnesium sulphate, and sometimes other impurities, are almost certain to be present. In the limited time at my disposal, I was unable to devise any satisfactory plan for the estimation of these impurities, and the tabulated results are, therefore, given without this correction.

In regard to the last example given ( No. 6 ), which was from the "mixed potash sample" sent out to chemists in this country and Europe, it may be said that the quantity taken,  $\frac{1}{4}$  gram, is too small for accurate work, as every error is, of course, quadrupled in the final result. These estimates were the last made, and lack of material prevented the employment of a larger quantity. As the results tally fairly well, however, with the work of others, they are given for what they are worth.

It will be observed that the "alternate" method is to a certain extent liable to the same objection as the Lindo-Gladding. Most of the loss here comes from the "occlusion" of potash in the barium sulphate. How seriously this affects the final estimate may be seen from the tabulated results given below.

A large amount of work done in the same line of investigation is omitted, but all leading substantially to the same results.

The six examples given are, indeed, selected from some twenty that were more or less fully carried out. Those taken are those in which the amount of loss by washings and precipitates is the lowest. In the course of the work some very anomalous results were obtained. In one case as high as thirty-four milligrams of potassium platinochloride were recovered from a barium sulphate precipitate weighing only 320 milligrams, and from which boiling water had ceased to dissolve out any more potash. Faulty manipulation may in some way have affected the result; but I think that any chemist who attempts to wade through the mass of work that I have gone over, and to unravel the singularly tangled skein of surface or molecular forces which govern the behavior of potash salts in the presence of barium sulphate and other precipitates, will meet with a good many surprises. He will find first of all, that the accredited statement of most chemical authorities that potash salts are not carried down by barium sulphate in acid

solutions, is altogether a fallacy. He will find that the amount carried down is subject to wide variations, and that, too, under conditions seemingly identical. He will probably come at last to the conclusion that this whole subject of the occlusion of potash salts by precipitates needs thorough and exhaustive investigation; and that until it is done and the losses resulting therefrom are eliminated, we must write "doubtful" after every potash determination made by processes involving this very obscure but very positive source of error.

ANALYSIS OF MIXED FERTILIZERS CONTAINING BONE, BLOOD, ETC., TOGETHER WITH THE SAMPLE OF MIXED POTASH SALTS SENT OUT BY THE "REPORTER" BY THE LINDO-GLADDING METHOD WITH ESTIMATES OF LOSSES OF POTASH IN PRECIPITATES AND "WASHINGS." MADE AT THE FLORIDA STATE LABORATORY, NORMAN ROBINSON, ANALYST.

Mixed Fertilizer.	Amt. of material used in grams.	Weight of $K_2PtCl_6$ by Lindo-Gladding Method.	Weight of $K_2PtCl_6$ recovered from precip. by Am. and Am. Ox.	Weight of $K_2PtCl_6$ recovered from first alcohol washing.	Weight of $K_2PtCl_6$ recovered from washing with $NH_4Cl$ solution with 2nd alcohol W.	Total weight of $K_2PtCl_6$ recovered from all sources.	Percentage of $K_2O$ by Lindo-Gladding Method.	Percentage with losses added.	Percentage of loss.
1—With Bone, Etc.	1	0.3263	0.0030	0.0041	0.0051	0.0122	12.60	13.07	0.475
2—With Bone, Etc.	1	0.4040	0.0041	0.0034	0.0061	0.0136	7.80	8.06	0.26
3—With Bone, Etc.	1	0.2433	0.0031	0.0021	0.0033	0.0085	4.70	4.86	0.16
4—With Bone, Etc.	1	0.2114	0.0028	0.0031	0.0053	0.0112	4.10	4.32	0.22
5—With Phos. R'k.	1	0.3160	0.0084	0.0033	0.0018	0.0135	12.20	12.72	0.52
6—Mixed Potash Salts.	1	0.4884	0.0031	0.0042	0.0022	0.0095	37.70	38.43	0.73

Average loss to each 1 per cent. of potash estimated by Lindo-Gladding method. 0.029

ANALYSIS OF SAME BY THE "ALTERNATE" METHOD WITH SIMILAR ESTIMATES OF LOSSES IN PRECIPITATES AND WASHINGS.

	Amount taken in grams.	$K_2PtCl_6$ by alternate method.	$K_2PtCl_6$ recovered from Am. and Am. Ox. precipitate.	$K_2PtCl_6$ recovered from $BaSO_4$ precipitate.	$K_2PtCl_6$ from alcohol washings.	Total $K_2PtCl_6$ recovered.	Per cent. of $K_2O$ by alternate method.	Per cent. with losses added.	Per cent of loss.
1.....	1	0.3268	0.0021	0.0061	0.0024	0.0106	12.63	13.04	0.41
2.....	1	0.3989	0.0015	0.0083	0.0036	0.0124	7.70	7.94	0.24
3.....	1	0.2331	0.0024	0.0063	0.0024	0.0111	4.50	4.70	0.21
4.....	1	0.2072	0.0010	0.0064	0.0033	0.0107	4.00	4.21	0.21
5.....	1	0.3056	0.0022	0.0073	0.0031	0.0126	11.80	12.29	0.49
6.....	1	0.4896	0.0015	0.0044	0.0038	0.0097	37.81	38.56	0.75

Average loss to each 1 per cent. of  $K_2O$  estimated by Alternate method. 0.29

*The Stassfurt or Anhalt Method.*—As our German friends are naturally very partial to the Stassfurt method of determining potash in potash salts, the writer was led to make some tests to determine whether the same or similar objections could be urged against it as are believed to lie against our American methods. Concerning this plan of estimating potash, it may be said that it is not likely to be popular until one acquires considerable facility in its use. The accurate precipitation of the sulphuric acid is pretty certain to give trouble at first. If, however, the precipitation be made in a vigorously boiling solution, this difficulty vanishes. The barium sulphate is then heavy and crystalline, and settles like so much sand. After considerable experience in its use the writer has come to prefer this German method to any other from the fact that it involves less manipulation, gives an unusually clean precipitate of potassium platinochloride, and generally requires less alcohol for washing. The writer is convinced, however that it is chargeable with the same essential defect as the Lindo-Gladding and the alternate methods. It does not estimate all the potash present. The barium sulphate manifests the same peculiarity here as elsewhere.

From a previous dissolved sample of the mixed German potash salts sent out by the reporter, 200 cc. was taken, corresponding to five grams of material, precipitated as accurately as possible with barium chloride and made after cooling to 251.25 cc., and after vigorous shaking set aside for a few hours to secure the complete subsidence of the barium sulphate. (The volume of the latter was determined at 1.25 cc. by calculation from the barium chloride used and confirmed by subsequent weighing.) Ten cc. accurately measured of the clear solution corresponding to one-fifth gram gave 0.392 of potassium platinochloride  $\times 5 = 1.960$  or 37.84 per cent., which closely approximate the average of the estimates made by German chemists; as much of the remaining liquid as could be moved without disturbing the precipitate was now poured off into a clean, dry beaker, and the precipitate with portions of this same solution was washed into an accurately calibrated fifty cc. measuring cylinder and again allowed to settle. After three hours the precipitate with the

mingled solution occupied a volume of sixteen cc. and did not seem inclined to go any lower. The clear liquid was now taken out with a pipette until exactly 21.25 cc. remained. The whole was now poured upon a dry nine cm. Schleicher and Schüll filter and exactly ten cc. filtered off and rejected. This of course left ten cc. of the solution and 1.25 cc. of the barium sulphate. The filter was repeatedly washed with hot water until no reaction was observable with silver nitrate. This last ten cc. of solution with the washings gave 0.4276 of potassium platinochloride or 22.6 mgms. more than the first ten cc. of solution examined, showing that this amount of potash was held up or occluded by the barium sulphate in a form that boiling water would remove. The filter with its precipitate was then boiled twice in twenty-five cc. dilute hydrochloric acid (one to five). In this way forty-four mgms. more potassium platinochloride were obtained. The total amount of potassium platinochloride recovered from the barium-sulphate precipitate was 66.6 mgms. or 0.01288 to each gram of substance = 0.247 per cent., or nearly one-fourth of one per cent. Other tests of the same material in smaller quantity gave considerably higher results, but as great care was taken to secure accuracy in every stage of the process, it is believed that the above fairly indicates the average loss where this particular material is estimated by the Stassfurt method. Much more extended investigations are required before any confident statements can be made as to the average loss from occluded potash when this method is employed.

Several other determinations exceeded this estimate. The instance given was carried out with special care. Full details of the methods used will be furnished to any one interested in the matter and perhaps not unfairly represents the average loss from this source.

In conclusion, it may be urged that, even conceding that there are some inherent defects in all our methods, since they are generally recognized and understood, and give fairly accurate results; anything looking towards a change is ill-timed and unwise. But what are we to consider "fairly accurate results?" As reporter on potash for the current year, the writer is compelled to echo an altogether too familiar refrain. We come up

here and, year after year, sing the same old tune. It is just as full of discord this year as it was last year and the year before that. To the question "How much potash?" working upon identically the same sample, New Hampshire says 12.13 per cent., New Jersey 12.76, New York and Maine 12.94, and North Carolina 13.08 per cent. and 13.22 per cent. Now here is a difference of considerably more than one per cent. in the same material, and that too, scattered along the whole gamut of rising estimates. Can these be considered "fairly accurate results?"

If we turn to our German friends, we find more unanimity but by no means complete agreement. Their answers to the same questions range from 13.10 per cent. to 13.44 per cent. Now who in this "confusion" of chemical tongues, has given us the right answer? Even on the face of it, is there not enough to suggest that there may be something wrong with the chemistry, as well as the chemists?

Notwithstanding the views and tabulated determinations above given, your reporter has no changes in existing methods to suggest. He only desires that the investigations he has outlined shall be submitted to careful re-examination, especially the "occlusion" of potash salts in precipitates, and that the relation of this as yet obscure phenomenon, to potash determination (a source of the error to which, so far as he is aware, the writer has now for the first time directed attention), should be made the subject of thorough investigation and review. If his conclusions are confirmed, changes are sure to come. Until then it seems the wiser course to adhere to existing methods.

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[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 4.]

### GANTTER'S PROCESS FOR DETERMINING THE IODINE FIGURE OF FATS.

BY PARKER C. MCILHINEY, PH.B., A.M.

Received March 31, 1894.

F. Gantter, (*Ztschr. anal. Chem.*, **32**, 178 and 181) proposes a new method of determining the iodine figure of fats and oils in which he uses carbon tetrachloride as a solvent for both the fat and iodine and uses no mercuric chloride as in the Hübl pro-

cess. He states that the figures obtained when mercuric chloride is used depend upon the amount used. The results which he obtained and from which he draws these conclusions are as follows:

Substance.	Amount iodine used.	Amount HgCl <sub>2</sub> used.	Iodine figure.
0.100 gram linseed-oil....	0.100 gram.	0.050 gram.	83.5
" " " " ....	0.600 "	0.000 "	85.3
" " " " ....	0.150 "	0.250 "	141.0
" " " " ....	0.150 "	0.500 "	148.0
" " " " ....	0.600 "	0.250 "	156.4
" " " " ....	0.600 "	0.500 "	173.6
" " " " ....	0.600 "	1.000 "	188.4
" " lard .....	0.500 "	0.000 "	25.0
" " " .....	0.500 "	0.250 "	61.0
" " " .....	0.500 "	0.500 "	63.0
" " " .....	0.500 "	1.000 "	85.1

His results prove that the amount of mercuric chloride present influences the results and that a very large excess of Hübl's reagent would give a higher figure for linseed-oil than a moderate excess, but they certainly do not justify the conclusion which he draws from them that the use of mercuric chloride is unnecessary, and it is on this assumption that the accuracy of his process depends.

To ascertain whether fats would absorb from a solution of iodine alone in any suitable solvent as much iodine as would be necessary to convert them into saturated bodies, portions of a sample of oleic acid were treated with measured quantities of solutions of iodine in alcohol, carbon disulphide, and carbon tetrachloride. All these solvents dissolve both the oleic acid and iodine.

The results were as follows:

Solvent.	Amount of oleic acid.	Excess of iodine in cc. $\frac{N}{10}$ thio-sulphate.	Iodine figure.
Alcohol.....	0.9947 gram.	43.4	30.4
" .....	1.1445 grams.	43.5	26.1
Carbon disulphide ...	0.9791 gram.	58.9	52.7
" " ...	1.0044 grams.	59.0	51.3
Carbon tetrachloride.	0.1171 gram.	27.9	27.6
" " .....	0.1186 gram.	28.2	24.1

The iodine figure of the sample as determined by the Hübl process was 80.0.

These results show that iodine alone will not saturate fats and if it is used for this purpose its action must be assisted by mercuric chloride. Gantter's process, therefore, does not determine the iodine figure but an arbitrary figure which is not comparable with the results obtained by any other process.

## THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(Concluded from Page 332.)

BY THOMAS B. STILLMAN, PH.D.

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STEVENS INSTITUTE OF TECHNOLOGY, DECEMBER, 1893.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 5.]

## THE QUANTITATIVE SEPARATION OF ROSIN OIL FROM MINERAL OILS.

BY PARKER C. McILHINEY, Ph.B., A.M.

Received March 31, 1894.

These two oils being both unsaponifiable are usually determined together as "unsaponifiable material" in the analysis of oils. They may be distinguished from one another by several methods.

1. *The Specific Gravity*.—Rosin oil has a much higher gravity than mineral oils, varying from 0.960 to 1.000 while heavy mineral oils range from 0.850 to 0.920.

2. *Valenta's Test*.—*Dingler's Poly. J.*, **252**, 297, and **253**, 418, *J. Chem. Soc.*, **48**, 93. Glacial acetic acid dissolves 2.67–6.50 per cent. by weight of mineral oil while rosin oil is soluble to the extent of 16.87 per cent. Mixtures, however, do not dissolve in proportion to the amount of rosin oil present.

3. *The Stannic Bromide Test*.—Allen, *Comm. Org. Anal.*, **2**, 463. A solution of stannic bromide in carbon disulphide gives, with small quantities of rosin oil in carbon disulphide solution, a purple coloration, while mineral oils do not.

4. *Solubility in Acetone*.—Demske and Morawski, *Dingler's Poly. J.*, **258**, 39. Acetone is miscible with rosin oil in all proportions while mineral oils require several volumes for solution.

5. *The Elaidin Test*.—Hager, *Ztschr. anal. Chem.*, **19**, 116. Rosin oil gives a dark red clear liquid while mineral oils remain unchanged.

6. *Ammonia Emulsion Test*.—Hager, *Muspratt's Tech. Chemie.*, **1893**, **4**, 127, mixes two cc. of the oil to be tested with two cc. of petroleum benzine and four cc. of water and after shaking adds one cc. of ten per cent. ammonia; he then shakes violently and allows to stand for one to two hours. A persistent milky layer indicates rosin oil.

7. *Action of Sulphuric Acid*.—Hager, *Ztschr. anal. Chem.*, agitates a portion of the oil with an equal volume of concentrated sulphuric acid for five minutes and then pours into several volumes of cold water. Mineral oil gives a white milky liquid which separates into two clear light-colored layers. Rosin oil gives a gray or brownish milky liquid which separates an upper layer of yellow-brown color full of opaque flocks.

8. *The Color Produced with Sulphuric and Acetic Acids*.—Storch, *Analyst*, **13**, 71. Two cc. of the oil is shaken up with one cc. of anhydrous acetic acid and warmed gently. After cooling, the acetic liquid is removed with a pipette and a drop of strong sulphuric acid added which immediately produces a brilliant red color if any rosin oil is present. Cholesterin in many fatty oils gives a similar reaction. The same author determines rosin oil

quantitatively by its solubility in alcohol which is expected that of mineral oils.

9. *The Hübl Figure*.—Valenta, *Dingler's Poly. J.*, 1895, 295, 296. The Hübl figure of rosin oil is forty-three to forty-eight arches, that of mineral oils is below fifteen.

10. *The Refractive Index*.—Holde, *Mittheil. d. chem. tech. Anst.*, 1890, 8, 269. With the Abbe refractometer the results are as follows:

Rosin oil.....	1.5344
Mineral oils.....	1.4923

11. *Maumene's Test*.—*Muspratt Tech. Chem.*, 1893, 4, 127. In Rosin oil gives a rise of temperature of 42° C. Mineral oil shows a slight rise. Allen, *Comm. Org. Anal.*, 2, 462, says the temperature of rosin oil is 18°–20° C.

12. *The Action of Nitric Acid*.—*Muspratt*, 4, 127. Nitric acid of 1.185 sp. gr. when heated with rosin oil reacts violently with it giving off copious red fumes while mineral oils are but slightly effected.

Allen, *Comm. Org. Anal.*, 2, 462, says that cold nitric acid is sometimes without immediate action on rosin oil but on warming a violent reaction often very suddenly ensues and after cooling, the rosin oil is found to have been converted into a more or less brittle red resin.

This process was investigated with a view to making it quantitative. Attempts were made to use nitric acid of 1.42 sp. gr. at a boiling temperature, but the frothing of the mass proved a serious difficulty, the liquid in every instance frothing out of the flask. Acid of 1.2 sp. gr. was found more manageable, the frothing in this case being slight. It was thought that the red resin might be dissolved in alkali, in which it appears to be quite soluble, and leave behind the mineral oil which could be dissolved in benzine, but this process could not be made to work satisfactorily. It was found, however, that the red resin produced from the rosin oil was insoluble in petroleum ether while mineral oil dissolves easily.

The process was therefore altered by diluting the products of the reaction with water and extracting with petroleum ether.

The following process gave satisfactory results:

cc. of nitric acid of 1.2 sp. gr. are heated to boiling in a 700 cc. capacity. The source of heat is removed and less than 10 cc. of the oil to be analyzed added. The flask is then placed on the water-bath, with frequent shaking, for fifteen to twenty minutes, and about 400 cc. of cold water added. After the liquid has become entirely cold, fifty cc. of petroleum ether is added and the flask agitated. The oil which remains external upon dissolves in the ether, while the resin remains in suspension. The liquid is poured into a tapped separator, leaving about 10 cc. of solid resin as far as possible behind in the flask. After settling, the aqueous liquid is drawn off and the ethereal liquid poured into a tared flask. Another portion of petroleum ether is added to the resin remaining in the flask and allowed to act upon it for about ten minutes, when it is added to that in the tared flask. After distilling off the ether the oil is weighed. Mineral oils lose about ten per cent. in this way, and hence the weight of oil found must be divided by 0.9 in order to find the amount present in the sample analyzed.

Allen found mineral oils to lose ten to twelve per cent. on treatment with nitric acid. *Pharm. Jour.*, [3], 11, 266.

A mixture of seventy-six per cent. of mineral oil with twenty-four per cent. of rosin oil gave, by this method, 76.8 per cent. of mineral oil.

## RUTHENIUM AND ITS NITROSOCHLORIDES.<sup>1</sup>

BY JAMES LEWIS HOWE.

A FEW years ago A. Joly<sup>2</sup> published the results of an investigation on the supposed tetrachloride of ruthenium of Claus, in which he showed that the double salts of this compound, the "red salt" of Claus, are in reality double salts of a nitrosochloride,  $\text{RuCl}_2\text{NO}$ . When his work came to my notice I was engaged in studying the compounds of ruthenium, especially seeking to discover a simple and certain way of forming the supposed tetrachloride. Being engaged at present on other compounds of ruthenium, I present in this paper results reached,

<sup>1</sup> Read before the Cincinnati Section, March 15, 1894.

<sup>2</sup> *Compt. rend.*, 107, 998; 108, 854.

chiefly respecting the nitrosochlorides. For the unexpected formula of these compounds I am indebted to Joly, as at the time of his publication I had not analyzed any of the compounds; the rest of the work was entirely independent of his researches, and in the cases where the same work has been carried out by each of us, his results are in every respect confirmed.

The crude ruthenium was purified by fusion with caustic potash and saltpeter, and distillation of the dissolved melt in a stream of chlorine, as  $\text{RuO}_4$ . Good results were also obtained by treating the solution of the melt with potassium permanganate and sulphuric (or nitric) acid in the retort, and distilling. In either case the  $\text{RuO}_4$  was received in dilute alcoholic potash. When the precipitate, or that obtained by treating a solution of the melt with nitric acid, is boiled for several days with aqua regia, in a flask provided with a return condenser, the ruthenium is completely converted into the nitrosochloride. (In his first paper Joly describes the formation of the nitrosochloride by treatment of  $\text{RuCl}_3$  with a nitrite, and in his second paper by treatment with a large excess of nitric acid.) The solution in aqua regia is evaporated to dryness on a water-bath, the residue dissolved in water and treated with the chloride on an alkali; the corresponding double chloride then crystallizes out, either directly or on evaporation of the solution. The following salts have been studied, the analyses of the potassium and ammonium salts being given merely in confirmation of Joly's results.

1. *Potassium Ruthenium Nitrosochloride, or Potassium Nitrosochlorruthenate.*  $2\text{KCl}, \text{RuCl}_3\text{NO}$ , or  $\text{K}_2\text{RuCl}_3\text{NO}$ .—Formed by direct precipitation of very concentrated solutions of  $\text{RuCl}_3\text{NO}$  with  $\text{KCl}$  solution, or by evaporation of the mixed solutions. The analyses, as well as those of the other salts, were made by heating the salt in a stream of hydrogen and collecting the hydrochloric acid evolved in a solution of silver nitrate. The nitrogen of the  $\text{NO}$  group is reduced and deposited in the cooler portion of the combustion tube as ammonium chloride. Claus' analytical error, which led him to the formula  $2\text{KCl}, \text{RuCl}_3$ , was in not directly estimating the evolved chlorine, the loss  $\text{Cl}_2\text{NO}$  differing very slightly in weight from  $\text{Cl}_2$ .

## ANALYSIS.

	Calculated.	Found.	
		I.	II.
Cl <sub>2</sub> NO (loss).....	34.98	34.77	34.38
Cl <sub>2</sub> .....	27.27	26.98	27.07
NO (difference).....	7.71	7.79	7.30
Ru .....	26.77	26.65	25.99
2KCl .....	38.24	38.41	....
Cl <sub>2</sub> (in 2KCl) .....	18.18	....	18.62

## SOLUBILITY.

At 25°..... 100 parts water dissolve 12 parts salt.

At 60°..... " " " " 80 " "

2. *Ammonium Ruthenium Nitroschloride.* 2NH<sub>4</sub>Cl, RuCl<sub>2</sub>NO.  
—Formed as above from RuCl<sub>2</sub>NO and NH<sub>4</sub>Cl.

## ANALYSIS.

	Calculated.	Found.
Cl <sub>2</sub> .....	50.96	50.34
Ru .....	30.02	29.61

## SOLUBILITY.

At 25°..... 100 parts water dissolve 5 parts salt.

At 60°..... " " " " 22 " "

3. *Rubidium Ruthenium Nitroschloride.* 2RbCl, RuCl<sub>2</sub>NO and 2RbCl, RuCl<sub>2</sub>NO, 2H<sub>2</sub>O.—When very concentrated solutions of RuCl<sub>2</sub>NO and RbCl are mixed there is precipitated a small amount of rather pale-purple anhydrous salt. If solutions less concentrated are mixed and evaporated over sulphuric acid, the hydrated salt crystallizes out in large crystals, accompanied by some of the anhydrous salt. On evaporating a solution of the hydrated salt to dryness on the water-bath, or even on heating its solution, it is almost completely converted into the anhydrous salt.

*a. Anhydrous Salt.*—Fine pale-purple powder, which may be recrystallized from hot water in small, almost black crystals, closely resembling the potassium and ammonium salts, and which, like these, give a pale-purple powder in the mortar.

## ANALYSIS.

	Calculated.	Found.	
		I.	II.
Cl <sub>2</sub> NO (loss).....	28.27	.....	28.13
Cl <sub>2</sub> .....	22.04	.....	21.89
NO (difference).....	6.23	.....	6.24
Ru .....	21.64	.....	21.35
2RbCl (Rb=85.2) ..	50.09	.....	50.52
Ratio Ru:2RbCl....	I : 2.314	I : 2.294	....
Ratio Ru : Cl <sub>2</sub> .....	I : 1.018	I : 1.017	....

(I was a mixture of anhydrous and hydrated salt.)



## SOLUBILITY.

At 25°..... 100 parts water dissolve 0.57 parts salt.

At 60°..... " " " " 2.13 " "

*b. Hydrated Salt.*—Large dark-purple crystals, losing their water of crystallization very readily over sulphuric acid, and difficult to completely free from the adhering anhydrous salt.

## ANALYSIS.

	Calculated.	Found.	
		I.	II.
$\text{Cl}_2\text{NO}$ , $2\text{H}_2\text{O}$ (loss) .....	33.26	31.70	32.43
$\text{Cl}_2$ .....	21.51	20.83	19.42
NO (difference).....	5.79	NO and $2\text{H}_2\text{O}$ } 10.87	NO 5.98
Ru .....	20.13		19.75
$2\text{RbCl}$ .....	46.60	47.	....
$2\text{H}_2\text{O}$ .....	6.96	....	7.03

(I had lost some water by standing over sulphuric acid before the first weighing was made.)

## SOLUBILITY.

At 25°..... 100 parts water dissolve 114.3 parts salt.

4. *Cesium Ruthenium Nitrosochloride.*  $2\text{CsCl}$ ,  $\text{RuCl}_2\text{NO}$  and  $2\text{CsCl}$ ,  $\text{RuCl}_2\text{NO}$ ,  $2\text{H}_2\text{O}$ .—As with the rubidium salts, when very concentrated solutions of  $\text{RuCl}_2\text{NO}$  and  $\text{CsCl}$  are mixed, cesium ruthenium nitrosochloride is partly precipitated as the anhydrous salt, while on evaporating the less concentrated cold mixed solutions over sulphuric acid, large crystals of the hydrated salt are formed. Some of the anhydrous salt is usually formed at the same time, even in the cold. On evaporating a solution of the very soluble hydrated salt on the water-bath to dryness, it is completely changed into the very slightly soluble anhydrous salt. I have not found it possible to form the hydrated salt from the anhydrous, nor to obtain the anhydrous salt in crystals large enough to be seen by the naked eye.

*a. Anhydrous Salt.*—Fine pale-purple powder, not differing in appearance from the rubidium salt, but less soluble.

## ANALYSIS.

	Calculated.	Found.		
		I.	II.	III.
$\text{Cl}_2\text{NO}$ (loss) .....	23.61	23.85	....	23.56
$\text{Cl}_2$ .....	18.41	17.93	18.19	18.41
NO (difference) .....	5.20	5.92	....	5.15
Ru .....	18.08	17.62	....	17.85
$2\text{CsCl}$ ( $\text{Cs} = 132.7$ ).....	58.31	58.40	....	57.90

## SOLUBILITY.

At 25° ..... 100 parts water dissolve 0.20 parts salt.

At 60° ..... " " " " 0.56 " "

*b. Hydrated Salt.*—Large dark-purple crystals, often ten millimeters long or broad. Loses water of crystallization readily over sulphuric acid.

## ANALYSIS.

	Calculated.	Found.
$\text{Cl}_4\text{NO}, 2\text{H}_2\text{O}$ (loss) .....	28.10	28.11
$\text{Cl}_3$ .....	17.32	16.92
$\text{NO}$ (difference).....	4.90	5.59
$\text{Ru}$ .....	17.01	16.63
$2\text{CsCl}$ .....	54.88	55.13
$2\text{H}_2\text{O}$ .....	5.87	5.60

## SOLUBILITY.

At 25° ..... 100 parts water dissolve 105.8 parts salt.

The properties of the nitrosochlorides agree almost, if not completely, with those ascribed to ruthenium tetrachloride by Claus<sup>1</sup> and M. C. Lea.<sup>2</sup> The most remarkable property, to which Joly has also called attention, is their stability.

Two and four-tenths grams of the potassium salt was heated with gradually increasing temperature in an air-bath. Up to above 250° the loss was less than 0.5 per cent. Direct heat was then applied to the crucible till the salt was partially decomposed,  $\text{Cl}$  and  $\text{NO}$  being evolved. The whole was then treated with water, and from the soluble portion the original undecomposed salt was crystallized. No trace of ruthenium trichloride was present, showing that the  $\text{NO}$  is not given off until the chlorine also passes off.

The solutions of the nitrosochlorides are unacted on by urea in acid or alkaline solutions, nor are they reduced by  $\text{FeSO}_4$ ,  $\text{Cu}_2\text{Cl}_2$ , or  $\text{SnCl}_2$ . Hydrogen dioxide has no effect in acid solutions; in alkaline solutions oxygen is evolved, the solution becoming decolorized, but the change appears to be the same as that when the original solution is treated with excess of alkali.

Potassium permanganate has no reaction in acid solutions, but in alkaline solutions (with fixed alkalies) on boiling the green color of the manganate appears, soon followed by the

<sup>1</sup> *Bull. de l'Acad. Imp. de St. Pet.*, 1, 107; 4, 457.

<sup>2</sup> *Am. J. Sci.*, 38, 81, 248.

brown precipitate of the hydroxide, and the ruthenium salt is reduced to its trivalent condition. The solution after the reaction, gives the test for nitric acid, which is not the case with the original solution. It is then probable that the NO group is oxidized off by the permanganate.

Sodium hypobromite also reacts with the nitrosochloride in the cold, with evolution of gas; on acidifying with hydrochloric acid,  $\text{RuO}_3$  is evolved with the bromine, a reaction analogous to the characteristic reaction of the trichloride with potassium chlorate and hydrochloric acid.

Potassium ferrocyanide gives no reaction in the cold with the nitrosochloride, but when *neutral* on boiling the solution becomes intensely deep brown, almost opaque unless very dilute. In acid solutions this reaction does not take place. Alkaline solutions become amber on boiling, but on careful neutralization with hydrochloric acid the brown coloration appears. An excess of acid changes the brown to a much less dense olive green, very different from the bright green produced by the trichloride with the ferrocyanide.

Sulphur dioxide has little effect in the cold, but when led into the warm alkaline solution of the nitrosochloride the solution gradually loses its rose color and becomes amber, and a precipitate is formed, very slightly soluble in water.

Potassium cyanide decolorizes the solution of the nitrosochloride on warming and a double salt seems gradually to be formed.

Oxalic acid has no apparent effect.

These last three reagents all have decided reactions with the trichloride and are now being further studied.

In the solutions of the heavy metals I have obtained no precipitates with the nitrosochloride, except with mercurous salts and those of silver. In both these cases a buff precipitate is thrown down, but on heating with nitric acid it is decomposed, the ruthenium passing into solution, the silver or mercurous chloride being left. Lead salts do not precipitate the nitrosochloride.

Copper sulphate gives no reaction, but on warming with excess of caustic alkali the copper hydroxide passes into solution, giving the azure-blue characteristic of Fehling's solution. From this, cuprous oxide is precipitated on warming with grape sugar.

When NO is led into a solution of ruthenium trichloride a change takes place, and the solution no longer gives the reactions for the trichloride; nor does it appear to contain the nitrosochloride. Differential characteristics for the nitrosochloride solutions as compared with the trichloride are the following:

Solutions rose becoming salmon pink on dilution.

No precipitate with excess of alkali.

No purple color on boiling with potassium thiocyanate.

No reaction with ammonia and sodium thiosulphate.

Deep brown on boiling with potassium ferrocyanide in neutral solution.

This last reaction is most characteristic.

Several attempts have been made by me to prepare a higher ruthenium chloride than the trichloride, but unsuccessfully.

$\text{RuO}_4$  dissolved in hydrochloric acid, yields on standing only  $\text{RuCl}_3$ ; the same is true of  $\text{RuO}_4$  dissolved in chlorine water.

$\text{RuS}_2$  was oxidized with  $\text{HCl}$  and  $\text{KClO}_4$ ; much of the ruthenium was volatilized as  $\text{RuO}_4$ , while the residue consisted solely of  $\text{RuCl}_3$ .

In order to prove conclusively that the "red salt" of Claus was the nitrosochloride it was formed according to the method used by Claus; *viz.*, oxidation of  $\text{RuS}_2$  with nitric acid.

#### ANALYSIS.

	Calculated.	Found.
$\text{Cl}_3$ .....	26.77	26.95

It seems at first sight entirely unexpected that we should find the group NO directly connected with a metal, but it is by no means unique. The affinity of ferrous salts for NO is familiar, and there are several comparatively stable compounds in which the group NO appears to be attached to iron, as the nitroso-pentasulphide and nitrosoheptasulphide, and the nitrosothiocarbonate. In the nitroprussides the NO group replaces in part the CN of the ferrocyanides. Iron and ruthenium occupy analogous positions in the periodic system, and as osmium is the third member of the series we should expect to find a similar and strong affinity of osmium for NO; indeed, Joly<sup>1</sup> has proposed to show that the osmiamic acid of Fritzsche and Struve has an

<sup>1</sup> *loc. cit.*

analogous constitution to the nitrosocompounds of ruthenium.

POLYTECHNIC SOCIETY, LOUISVILLE, KY.,  
March, 1894.

ON THE CRYSTALLIZATION OF  $2\text{CsCl}$ ,  $\text{RuCl}_3\text{NO}$ ,  $2\text{H}_2\text{O}$  AND  
 $2\text{RbCl}$ ,  $\text{RuCl}_3\text{NO}$ ,  $2\text{H}_2\text{O}$ .

BY N. D. CLARK.

These salts are isomorphous and crystallize in the monoclinic system. They show a similar habit and the crystals of both salts that were submitted for examination measured as much as ten millimeters in length.

The forms which were identified are

$a$ , 100, $i-\bar{i}$	$m$ , 110, $I$	$e$ , 101, $-I-\bar{i}$
$c$ , 001, $O$	$d$ , 021, $2-\bar{i}$	$o$ , 101, $I-\bar{i}$

The habit is prismatic like Figs. 1 and 2, while Fig. 3 represents a basal projection of Fig. 2. Of the forms in the prismatic zone  $m$  is always prominent while  $a$  is small and frequently fails. The prevailing forms that terminate the prisms are  $d$  and  $o$ , while  $c$  and  $e$  are usually either small or altogether wanting.

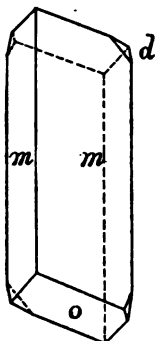


FIG. 1.

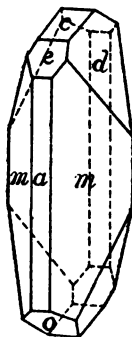


FIG. 2.

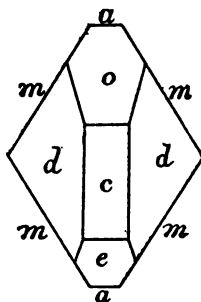


FIG. 3.

The axial ratios that are given beyond were calculated from the measurements that are marked by asterisks in the accompanying tables; the values cannot be regarded as very exact, as the crystal faces were slightly rounded and not adapted for accurate measurement. On the cesium salt the error in the fundamental measurements is regarded as not exceeding  $\pm 8'$ , while with the rubidium salt the error may exceed twice that amount.

		$a : b : c$			
$2\text{CsCl}, \text{RuCl}_3\text{NO}, 2\text{H}_2\text{O}$	1.698 : 1 : 1.177	$\beta = 76^\circ, 11'$			
$2\text{RbCl}, \text{RuCl}_3\text{NO}, 2\text{H}_2\text{O}$	1.692 : 1 : 1.242	$\beta = 76^\circ, 50\frac{1}{2}'$			
	Measured.	Calculated.	Measured.	Calculated.	
	$2\text{CsCl}, \text{RuCl}_3\text{NO}, 2\text{H}_2\text{O}.$		$2\text{RbCl}, \text{RuCl}_3\text{NO}, 2\text{H}_2\text{O}.$		
$a \wedge c$	$100 \wedge 001$	$76^\circ, 11'^*$	.....	$76^\circ, 50', 30''^*$	.....
$c \wedge e$	$001 \wedge 101$	$30^\circ, 0'^*$	.....	$31^\circ, 18'$	$31^\circ, 28', 28''$
$d \wedge d$	$021 \wedge 02\bar{1}$	$132^\circ, 45'^*$	.....	$135^\circ, 4'^*$	.....
$m \wedge m$	$110 \wedge \bar{1}\bar{1}0$	$62^\circ, 13'$	$62^\circ, 27', 59''$	$117^\circ, 30'^*$	.....
$a \wedge m$	$100 \wedge 110$	$58^\circ, 45'$	$58^\circ, 46', 6''$	$58^\circ, 50'$	$58^\circ, 45'$
$m \wedge d$	$110 \wedge 021$	$33^\circ, 18', 30''$	$33^\circ, 35'$	.....	$33^\circ, 37', 33''$
$c \wedge o$	$001 \wedge \bar{1}01$	$38^\circ, 34', 30''$	$38^\circ, 53', 23''$	$39^\circ, 32'$	$40^\circ, 37', 9''$
$a \wedge e$	$100 \wedge 101$	$46^\circ, 12'$	$46^\circ, 11'$	$46^\circ, 6'$	$45^\circ, 22', 2''$
$d \wedge c$	$021 \wedge 001$	$66^\circ, 22', 30''$	$66^\circ, 30'$	.....	$67^\circ, 32'$
$a \wedge o$	$\bar{1}01 \wedge 100$	$65^\circ, 13', 30''$	$64^\circ, 55', 37''$	$63^\circ, 33'$	$62^\circ, 32', 21''$

Both salts show a perfect cleavage parallel to  $a$  and a poorer one parallel to  $c$ . The plane of the optical axes is the clinopinacoid; the double refraction is strong, and the optical orientation such that cleavage plates parallel to  $a$  show in convergent polarized light an optical axis almost in the center of the field.

This investigation was made in the mineralogical-petrographical laboratory of the Sheffield Scientific School, under the direction of Prof. S. L. Penfield, to whom the author's thanks are due.

### AN IMPROVED MERCURY THERMOMETER FOR HIGH TEMPERATURES.<sup>1</sup>

BY W. NIEHLS.

THE ordinary mercury thermometers give accurate values up to  $250^\circ \text{C}$ . When the thermometer tube above the mercury is filled with nitrogen under pressure, readings are possible up to  $450^\circ \text{C}$ .

Early in 1893 I submitted to the Physikalisch-Technische Reichsanstalt, at Charlottenburg, Berlin, which, as is well known, tests the correctness of normal thermometers, etc., models of high temperature thermometers which were capable of giving accurate readings up to  $550^\circ \text{C}$ . Since then minor details of construction have been satisfactorily completed, and in the following, I will briefly describe the perfected instrument.

<sup>1</sup> Read before the Cincinnati Section, April 16, 1894.

At the outset it was necessary to secure a variety of glass which does not soften below  $600^{\circ}$ . For this purpose the borosilicate glass of Jena was chosen and has shown itself well adapted in all cases. The graduation is brought directly on the tube, and ranges either from  $180^{\circ}$  to  $550^{\circ}$  in single degrees, or from  $100^{\circ}$  to  $550^{\circ}$  in intervals of five degrees. The scale is black, for the sake of the greatest clearness, and the method of its preparation is as follows: The thermometer tube is supplied with the requisite amount of mercury, and then completely filled with carbon dioxide under a pressure of twenty atmospheres. In this condition the tube is heated and graduated. The mercury is then removed, black enamel is rubbed in the scale, and the tube is introduced into a muffle where the scale is brought out clearly in enamel.

This treatment in the muffle has not only the advantage of yielding a permanent scale which resists strong acids, but it also brings about an artificial "ageing" or "seasoning" of the thermometer. In other words, it decreases in a marked degree, the tendency of a thermometer to give too high readings as time goes on. This is evident from the following experimental data:

Thermometers graduated to  $360^{\circ}$ , which showed ordinarily a rise of  $8^{\circ}$ – $10^{\circ}$ , gave, after this preliminary treatment, when heated for ten hours to  $340^{\circ}$ – $350^{\circ}$  an increase of but  $0.6^{\circ}$ – $0.8^{\circ}$ . Those graduated to  $400^{\circ}$  showed, under the same conditions, a rise of  $1.5^{\circ}$ – $2^{\circ}$ . In the case of thermometers graduated to  $550^{\circ}$  the rise under the same conditions was  $2^{\circ}$ – $3^{\circ}$ . After further heating for ten hours the rise was  $0.4^{\circ}$ – $0.6^{\circ}$ . On the contrary, thermometers graduated to  $550^{\circ}$ , but not exposed to the "seasoning" treatment, showed, after being heated for ten hours, a rise of  $16^{\circ}$ – $19^{\circ}$ , and after a further period of ten hours a rise of  $4^{\circ}$ – $6^{\circ}$ , while further increase was naturally to be expected.

A further improvement of the high temperature thermometer is the coating on the back of the tube which greatly facilitates readings. This same result has been secured in the construction of ordinary thermometers by introducing into the back of the tube a strip of enamelled glass. The difference in the coefficients of expansion renders this impossible in the case of the high temperature thermometers. The strip of enamelled glass has been

replaced, however, very satisfactorily by a simple coating of enamel which is fused upon the surface of the tube at the same time that the figures of the scale are produced. The enamel on the rear of the tube, as well as that of the graduation, are totally unaffected after prolonged exposure to high temperatures.

An extended use of these thermometers is to be expected not only in laboratories, but in many branches of chemical industry, such as tar works, petroleum refineries, anilin works, etc.

I would mention in this connection the great help I have experienced in using Mahlke's "thread thermometer" for obtaining accurate readings at high temperatures. This gives the proper correction for the error due to the projection of a part of the mercury column of the thermometer outside of the substance or confined space, the temperature of which is being measured. In the case of long thermometers and high temperatures this error may reach  $30^{\circ}$ . Mahlke's thermometer is hung alongside the projecting part of a thermometer in use, and is so arranged as to give at once the reading for the number of degrees to be added to the temperature indicated in order to correct the error mentioned.

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### ON THE ESTIMATION OF SULPHUR IN PYRITES.<sup>1</sup>

BY THOMAS S. GLADDING.

THERE are two recognized methods for the estimation of sulphur in pyrites which, with various modifications, are chiefly used by commercial chemists at the present time. These are:

First, the fusion of the ore with a mixture of sodium carbonate and potassium nitrate, solution in water, filtration from iron hydroxide, and precipitation as barium sulphate.

Second, the solution of the pyrites ore in aqua regia, or in aqua regia and bromine, and subsequent precipitation as barium sulphate.

The following investigation was undertaken to determine the relative merits of these two methods and the proper modifications to be observed:

A chemically pure potassium sulphate was examined for

<sup>1</sup> Read before the New York Section, March 9, 1894.



impurities with negative results. 2.7 grams containing about the amount of sulphur found in one gram of high grade pyrites were dissolved in 300 cc. to 400 cc. water, five cc. concentrated hydrochloric acid added, and a ten per cent. barium chloride solution added, at the rate of one drop per second, to the boiling solution. We obtained after standing over night:

Sulphur .....	0.4960 gram.
" .....	0.4960 "

Theory requires sulphur 0.4965. This amount of 0.496 gram was taken as the quantity of sulphur contained in 2.7 grams of the potassium sulphate, and the following series of experiments made exactly as above, with the stated additions and modifications. We first investigated the various conditions of the fusion methods.

Series I. With additions of five cc. nitric acid :

Sulphur found .....	0.5007 gram.
" " .....	0.5007 "
" " .....	0.5020 "

The presence of nitric acid produces results too high, from the dragging down of nitrate salts, probably barium nitrate.

Series II. With addition of seventeen grams potassium nitrate :

Sulphur found .....	0.5066 gram.
" " .....	0.5102 "

Series III. With addition of fifteen grams of fusion mixture; *viz.*, sodium carbonate and potassium nitrate, and addition of hydrochloric acid to neutrality and five cc. in excess :

Sulphur found .....	0.5005 gram.
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Series IV. With addition of potassium chloride, 6.5 grams, sodium chloride, seven grams :

Sulphur found .....	0.4955 gram.
" " .....	0.4950 "
" " .....	0.4966 "

No appreciable error either way.

The above series of experiments show that no *nitric* acid nor nitrates should be present in the solution at the time of precipitation. Series IV shows that when all nitric acid is expelled then sodium chloride and potassium chloride in solution will not cause error. We have found, however, that the complete expulsion of all nitric acid is a very difficult and tedious operation,

requiring repeated evaporations to dryness with excess of hydrochloric acid.

The practical difficulty of removing all the nitric acid, and time and labor required, are serious objections to this method.

The following experiments were made to investigate the conditions of the second or aqua regia method.

Series V. With addition of two grams of citric acid :

Sulphur found .....	0.4960 gram.
" " .....	0.4960 "

This shows that the citric acid, which is frequently used to keep up any iron present, does not exert a solvent action.

Series VI. With addition of two grams citric acid, and 0.500 gram iron, which is about the amount of iron in one gram of pyrites ore :

Sulphur found.....	0.4934 gram	-0.4937 gram.
" " .....	0.4937 "	-0.4933 "
" " .....	0.4940 "	-0.4937 "
" " .....	0.4938 "	.....

This shows that the presence of iron causes low results.

The above results were obtained by ignition of the barium sulphate precipitate at low red heat until the filter paper was thoroughly burned. The precipitate was of a buff color.

On exposing the precipitates to a strong blast for several minutes longer they assumed a decided red color and lost weight.

The results were found to be :

Sulphur found .....	0.4910 gram.
" " .....	0.4913 "
" " .....	0.4900 "

We attribute these erroneous results to the unavoidable dragging down of iron salts (probably iron sulphate) with the barium sulphate, and in place of an equivalent amount of barium sulphate. On ignition, this iron sulphate is decomposed, the sulphuric anhydride is expelled, causing low results, and the remaining iron oxide coloring the residue.

This was corroborated by taking 2.7 grams potassium sulphate, precipitating as above, drying the precipitate, brushing from the paper, drying at about 300° C., and adding the ash of the filter paper which had been burned in a separate dish.

Sulphur found .....	0.4961 gram.
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On heating over the blast-lamp for five minutes we found

Sulphur ..... 0.4880 gram.

It is evident that the presence of iron in the solution is incompatible with accurate results.

We next tried the method of Lunge and Hurter. They precipitate the iron with ammonia and throw down the barium sulphate in the filtrate.

Series VII. With addition of 0.5000 gram iron, precipitation of same with ammonia, and precipitation of barium sulphate in the filtrate:

Sulphur found ..... 0.4944 gram.

" " ..... 0.4935 "

These results were too low. On redissolving the ferric hydroxide (on filter paper) with hydrochloric acid, and adding barium chloride to the filtrate, and standing over night, we obtained a precipitate of barium sulphate, giving:

1. Sulphur ..... 0.0020 gram.

2. " " ..... 0.0021 "

Adding these amounts we obtained:

Sulphur ..... 0.4964 gram.

" " ..... 0.4956 "

The most careful washing failed to wash out all sulphur from the ferric hydroxide, and this solution in hydrochloric acid, and the separate recovery of sulphur contained therein, was found necessary.

These results were the most satisfactory yet obtained. The precipitate of barium sulphate was pure white, pulverulent and did not lose appreciable weight on prolonged heating over the blast-lamp. In this respect it differs from all precipitates hitherto obtained, demonstrates its far greater purity, and gives us a fixed and *final* result.

A method recently published instructs as follows: To the solution (about 200 cc.), heated on a steam-bath and containing twenty cc. free hydrochloric acid "add barium chloride solution from a burette, drop by drop, stirring briskly. Add thirty-five cc. and allow the solution to stand one hour on the steam-bath, filter through ten cm. paper and wash three times with hot water Ignite and weigh barium sulphate." After calculating per cent.

sulphur, add 0.20 per cent. to the result for solubility of barium sulphate in the acidified liquid.

We tested this method using 2.70 grams potassium sulphate, 200 cc. water, twenty cc. hydrochloric acid, and 0.500 gram iron. We obtained:

Sulphur .....	0.4900	gram.
" .....	0.4898	"
" .....	0.4902	"
" .....	0.4894	"
" .....	0.4905	"

The average loss was found to be about 0.60 per cent. instead of 0.20 per cent. as stated. The color of the precipitate was light buff. On heating over the blast-lamp for five minutes the precipitate assumed a darker color and lost 0.021 gram in weight so that the percentage of sulphur was reduced about 0.30 per cent. more. Evidently this method does not produce a pure precipitate of barium sulphate.

The following series of comparative analyses on samples of pyrites received for assay, corroborates the above results. The results given under "Fusion Method" were obtained *without* evaporating to dryness to expel all nitric acid. The results given under "Bromine Method, No. 1," were obtained by solution in nitric acid and bromine, evaporation to dryness with hydrochloric acid, taking up with hot water, plus hydrochloric acid, addition of two grams citric acid and precipitation without removing the iron.

In "Bromine Method, No. 2," the iron was removed with ammonia and the barium sulphate precipitated in the filtrate. The ferric hydroxide was dissolved in dilute hydrochloric acid in a separate beaker, heated to boiling, barium chloride added, allowed to stand over night, and the small amount of barium sulphate thus obtained added to the main precipitate.

Samples.	Fusion method.	Bromine method, Bromine method,	
		No. 1.	No. 2.
I .....	52.50	51.45	51.71
I .....	52.34	51.30	51.73
I .....	52.60	51.45	51.71
I .....	....	51.34	51.71
I .....	....	51.32	51.68
I .....	....	....	51.78

Samples.	Fusion method.	Bromine method,	
		No. 1.	No. 2.
2 .....	40.92	....	40.50
3 .....	39.90	39.25	39.60
4 .....	40.90	39.72	40.00
5 .....	41.25	40.05	40.40
6 .....	41.80	40.90	41.10
7 .....	40.59	39.71	....
8 .....	42.54	41.94	....
9 .....	41.41	40.40	....

We see from the above that the "Fusion Method" without expulsion of all nitric acid gives results altogether too high, as was to have been expected.

The "Bromine Method," when iron is not removed, gives results too low by 0.20 per cent. to 0.35 per cent. This is in exact agreement with the previous work on pure potassium sulphate. No accurate allowance can be made on this method as the error will vary with the amount of heat applied in igniting the precipitate of barium sulphate.

In the "Bromine Method, No. 2," the precipitated iron hydroxide was redissolved in every case, and an additional amount of sulphur varying from 0.20 per cent. to 0.30 per cent. was obtained.

The insolubility of barium sulphate in the solution of ferric chloride thus obtained was demonstrated by dissolving 0.027 gram potassium sulphate in fifty cc. water, adding five cc. hydrochloric acid and 0.5 gram iron, precipitating hot and allowing to stand over night. We found:

1. Sulphur.....	0.0049 gram.
2. " .....	0.0050 "
3. " .....	0.0051 "

The amount actually present was 0.00496 gram.

As a result of the above investigation and of many comparative analyses of pyrites ores extending over several years, we have adopted the following method of assaying pyrites:

1. Grind the ore to an impalpable powder, dry at 100° C., and keep in well-corked bottles. Ten to fifteen minutes drying is sufficient.

2. Weigh one gram, introduce into beaker, cover with watch-glass, and add ten cc. bromine solution, mix by rotating beaker

and allow to stand ten minutes in the cold. Add ten cc. nitric acid, mix as before, and allow to stand ten minutes longer in the cold. Finally place the beaker on a water-bath, containing cold water, heat slowly to boiling, and when solution becomes quiet remove glass after rinsing and evaporate to dryness. Add ten cc. hydrochloric acid, keeping the beaker covered with a glass, and when violent action ceases, again remove the glass after rinsing, and evaporate to dryness once more. Add one cc. concentrated hydrochloric acid and fifty cc. hot water, digest until solution is complete, filter and wash with hot water. The filtrate, about 100 cc., is now saturated with a slight excess of ammonia, allow to stand hot for ten minutes. The precipitated ferric hydroxide is filtered and washed five or six times more on the paper with boiling hot water, the filtrate acidulated with hydrochloric acid in slight excess, heated to boiling and fifty cc. barium chloride solution added, one drop per second to the boiling liquid. The solution is allowed to stand over night, filtered, washed, and ignited, the precipitate of ferric hydroxide is also dissolved in dilute hot hydrochloric acid heated to boiling, and ten cc. barium chloride solution added. It is allowed to stand over night and the barium sulphate thus obtained added to the main precipitate. One filter paper can be used for the two precipitates.

The bromine solution is prepared by dissolving seventy-five grams potassium bromide in fifty cc. water, adding fifty cc. bromine, stirring and adding water to 500 cc. The bromine will nearly all dissolve. Another form of bromine solution used by some is made by saturating aqua regia with bromine. The first solution is the more certain, however, to oxidize all the ore without separation of any sulphur. The barium chloride is in ten per cent. solution.

Thanks are due to our assistants, Mr. H. E. Cutts and Mr. Thomas Brown, for valuable assistance in the analytical work of the above investigation.

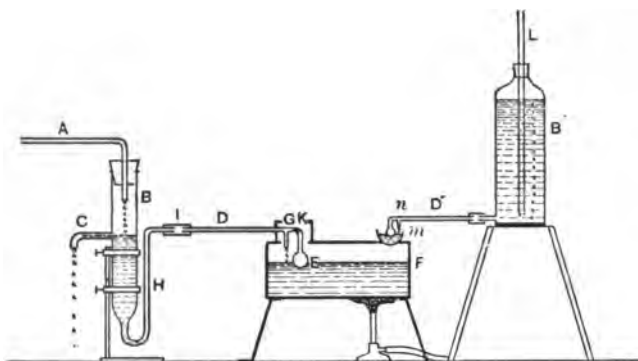
LABORATORY OF STILLWELL AND GLADDING,  
NEW YORK.

## A CONSTANT LEVEL APPARATUS.

By F. C. ROBINSON.

Received November 18, 1893.

THE following apparatus, which I have used for some time, may interest other chemists; hence the following sketch and description:



B is a glass tube about 2.5 cm. diameter into which is passed the small tube A through a cork. A side tube C extends out about ten cm. and is of much larger bore than A. Upon the lower end of B is sealed a small glass tube H which is bent up until opposite C, and then turned at right angles. Connected with H by a rubber tube is a tube D of equal bore and about twenty-five cm. long. Upon the other end of D is a bulb E, five cm. in diameter, turned down at right angles as shown in the cut. At the point G is a short tube and just beyond it at K, the tube D is closed up by melting it together. F is a water-bath through one of the openings of which E passes and floats upon the water. As the water rises in the bath, E, of course, floats higher, and raises the tube D. The rubber connector holds D upright and allows it to move. If B is clamped so that C and D are upon a level and the tap opened so that water flows into B through A, it will run out of both C and D, but of course D will soon float up so high that no water will run through it, and all will discharge at C. Now heat the bath and as soon as

evaporation has lowered D, sufficiently more water will run into the bath to take the place of that evaporated. A small stream of water flows constantly out at C and into the sink, but it need be very small indeed.

If the bulb E enters the bath through a place needed for evaporations, a small copper cylinder slightly larger than the opening and having a narrow strip cut out of it for D to move up and down in, may be placed over it as in the cut. Of course, the float may be placed in a side tube soldered to the bath with water-connection to it. If one cannot make it of glass it could easily be constructed of metal by any tinman.

I find also that the same idea works admirably for constant feeding of a small platinum dish in evaporating large quantities of water or other liquids for analysis of residues. In such cases the tube D' is directly connected with a bottle holding several liters of water in the manner illustrated in the cut at the right. As D' falls through evaporation of the water in *m*, air enters through L and water drops out at *n* till D' rises so that *n* is higher than the bottom of L, when it stops, and thus the level in *m* is constant. In this case the tube D' is very small so that the bulb can be very small and still hold it up. In the one I use, the bulb is only 1.5 cm. in diameter and the tube *n* so close to it that it can be used in a crucible. It is very easy to clean the float from the slight residue clinging to it at the end.

I use the same apparatus for washing precipitates with a large amount of water, placing the bulb in the funnel on the surface of the wash-water.

BOWDOIN COLLEGE,  
BRUNSWICK, MAINE, NOVEMBER 18, 1893.

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## A SCALE OF HARDNESS FOR GLASS.<sup>1</sup>

BY W. NIEHLS.

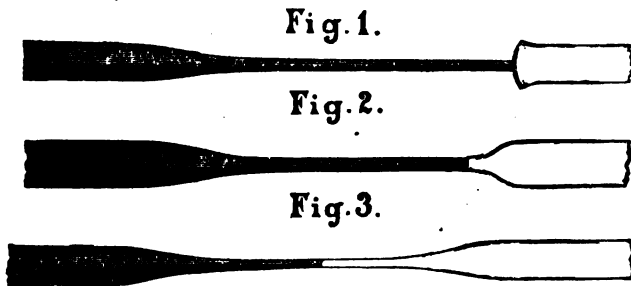
THE term "hardness" as applied to glass, refers to its degree of fusibility in the flame of the blast-lamp. Thus a glass which softens readily in the flame is called a "soft" glass, while one which softens with difficulty is called a "hard" glass. Between the extremes of a very soft and a very hard glass there

<sup>1</sup> Read before the Cincinnati Section, April 16, 1894.



is also quite a series of grades whose differences become very pronounced in actual glass working.

If this difference between two sorts be considerable it is impossible to effect permanent union by fusion between two samples. When the difference is slight, union may be effected between two sorts, but a condition of tension is produced which often causes later, a springing apart at the point of junction, even when not exposed to external strain. Permanent and satisfactory union is accomplished only when the varieties of glass are of the same, or nearly the same, hardness. Practiced glass-blowers make use of this fact in testing the sorts of glass placed at their disposal with reference to their power to unite. Samples of two sorts in the form of small rods are brought together evenly in a small pointed flame, heated therein uniformly, and when soft, fused together by pressure. They are then drawn slowly apart. The softer sample is drawn out more or less easily from the harder, so as to leave a quite pronounced edge when the difference in



hardness is considerable (Fig. 1).

When differences are less marked or are even quite slight, the different lengths of the drawn-out ends are quite noticeable and the dividing line between the two sorts is evident to the eye (Fig. 2).

If the two sorts are of the same hardness both ends are drawn out evenly and there is no line of demarcation (Fig. 3).

Hitherto there has been no systematic classification of glass varieties according to hardness for the convenience of commerce, industry, and science. This lack I have supplied by the arrangement—with the co-operation of the German Physikalisch-

Technische Reichsanstalt—of a well-defined scale of hardness for glass, divided into eight degrees. The following are the typical sorts of glass for each degree:

- I. The softest glass in commerce, French crystal.
- II. Soft Thuringian glass, used for artificial flowers, toys, etc., English crystal.
- III. Hard Thuringian glass, as used for thermometers, finer apparatus, etc.
- IV. Jena normal thermometer glass (XVI<sup>'''</sup> of Schott and Co.).
- V. French hard crystal used in Paris for normal thermometers (by Tonnelot).
- VI. Jena boro-silicate thermometer glass (59<sup>'''</sup> of Schott and Co.).
- VII. Jena thermometer glass free from alkalies (122<sup>'''</sup> of Schott and Co.). Both VI and VII are used for high temperature thermometers and many other purposes.
- VIII. Cavalier's Bohemian crystal glass, used for combustion tubes, etc.

Normal scales of hardness for glass, arranged according to the above scheme, have been prepared and can be secured through dealers in chemical apparatus. They contain on cardboard, illustrative samples of the results of fusing (as described above), each number in the series with the next following number. Compartments also are well stocked with small rods of each degree on the scale—each rod stamped with its number—to be used for testing.

The use of such a scale brings a most desirable element of certainty into the glass trade as well as into the technique of physical and chemical laboratories, and many industrial operations.

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[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 6.]

### A METHOD OF DETERMINING THE KOETTSTORFER FIGURE OF DARK-COLORED SUBSTANCES.

BY PARKER C. MCILHINEY, PH.D., A.M.

Received May 5, 1894.

THE Koettstorfer figure of a fat or resin is the number of milligrams of potassium hydroxide required to saponify one gram of the substance. It is determined by adding to a

weighed quantity of the substance a measured excess of an alcoholic solution of potash, evaporating off the alcohol, redissolving in neutral alcohol, and determining the excess of potash by standard hydrochloric acid. When the substance is light in color and the alcohol free from aldehyde, the determination is easily made, but if the substance has much color of its own the end reaction with phenolphthalein is indistinct. The same is true if the alcohol used contains aldehyde, as this gives with caustic potash a red-brown color. The latter difficulty can be surmounted by purifying the alcohol, but the former one is more serious. In experimenting to find a mode of procedure which would obviate the difficulty it was observed that a solution of neutral soap, to which ammonium chloride had been added, when submitted to distillation liberated a quantity of ammonia equivalent to the alkali combined with the soap.

Based on this principle the following method was devised: Two grams of the substance under examination is weighed into an Erlenmeyer flask, an excess of an alcoholic solution of caustic soda added, and the alcohol evaporated off. 250 cc. of ninety-three per cent. alcohol is now added and the solution heated until the soap is dissolved. Carbonic acid gas is now passed through the solution for about one hour. This treatment converts the free caustic alkali present into carbonate and bicarbonate which precipitate. The solution is then filtered into a suitable flask and most of the alcohol distilled off. It is necessary to add a spiral of platinum wire or a piece of sharp pointed metal or glass to prevent boiling over. When most of the alcohol is gone a solution of ten grams of ammonium chloride, in 100 cc. of water, is added and the solution distilled as far as possible, the distillate being caught in twenty cc. of normal hydrochloric acid which is titrated at the end of the operation, using methyl orange as indicator. The amount of hydrochloric acid neutralized by ammonia is equivalent to the combined alkali in the test.

Alcohol of ninety-three per cent. was found to dissolve sodium bicarbonate sufficient to neutralize 0.34 cc. of normal acid for every 100 cc. of alcohol used. A deduction must therefore be made for this in the calculation.

A sample of linseed-oil tested in this way gave a Koettstorfer

figure of 192.4, and by the ordinary process the figure found was 193.1. A sample of dragon's blood resin gave 124.9.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY  
OF CINCINNATI. XLV.]

### ON THE VOLATILITY OF BORAX.<sup>1</sup>

BY SIGMUND WALDBOTT, PH.D.

THE fact that borax is a volatile substance under ordinary laboratory conditions seems to have, hitherto, escaped notice. No reference is made to it in the literature of pure chemistry, and the following quotation from E. Cramer<sup>2</sup> would imply a general belief among technical chemists to the contrary:

"The boric acid must not be added in the form of vitreous boric acid, but in the form of sodium borate, whereby no volatilization will take place."

In the course of an investigation on the borates, carried on in connection with Prof. T. H. Norton, certain observations led to the suspicion that borax was not entirely unaffected by the heat of the ordinary blast-lamp.

A series of quantitative experiments was made, the results of which may be briefly summarized as follows:

If a small amount of pure borax, say four grams, be heated in a platinum crucible of fifty cc. contents, until the water of crystallization is quantitatively given off, and if the residue, borax glass, then be heated over a Bunsen burner for about ten minutes or longer, the weight will be found constant. If the crucible, half covered by the lid, be next heated over a gentle blast-flame, there will be noticed a very slight, yet distinctly perceptible loss in weight, increasing in proportion to the intensity of heat and the time of heating.

If now the uncovered crucible with its contents be subjected to an intense white heat, heavy vapors arise from the surface of the molten borax glass, and if heating is prolonged a very marked decrease in weight becomes evident.

The following experimental results are classified according to the general temperature maintained:

<sup>1</sup> Read before the Cincinnati Section, February 15, 1894.

<sup>2</sup> E. Cramer, *Thonindustrie-Zeitung*, 1892, p. 155.

## A. VOLATILITY AT HIGHER TEMPERATURES.

The experiments recorded under this heading were all carried out at a white heat, as high a temperature as could be obtained by the ordinary laboratory blast-lamp. The borax used in these experiments, unless expressly stated otherwise, was purified by recrystallization and by drying for about twelve hours on unglazed porcelain.

## I.

1.2500 grams  $\text{Na}_2\text{B}_4\text{O}_{10} + 10\text{H}_2\text{O}$ , when heated, lost 0.5968 gram  $\text{H}_2\text{O}$  = 47.74 per cent. (Theoretical loss = 47.12 per cent., drying on unglazed porcelain was omitted.)

0.6532 gram borax glass remained and was heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
5	Crucible uncovered .....	0.0055	0.0055	0.8
7	" covered .....	0.0010	0.0065	1.0
10	" uncovered .....	0.0060	0.0125	2.0
7	" half covered, chimney used	0.0039	0.0164	2.5
10	" uncovered .....	0.0054	0.0218	3.3
5	" " .....	0.0050	0.0268	4.1
2	" " .....	0.0009	0.0277	4.2

0.6532 gram borax glass lost 4.2 per cent. in forty-six minutes.

## II.

7.9201 grams  $\text{Na}_2\text{B}_4\text{O}_{10} + 10\text{H}_2\text{O}$ , when heated, lost 3.7356 grams  $\text{H}_2\text{O}$  = 47.17 per cent. (Theoretical loss = 47.12 per cent.)

4.1845 grams borax glass remained and were heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
5	Crucible open .....	0.0085	0.0085	0.23
10	" half covered .....	0.0040	0.0125	0.298
10	" " chimney used	0.0045	0.0170	0.406
	Lid, covered with drops, was heated	0.0023	0.0193	0.461
10	Crucible open .....	0.0080	0.0273	0.652
10	" " .....	0.0076	0.0349	0.834

4.1845 grams borax glass lost 0.83 per cent. in forty-five minutes.

In comparing the results of these two experiments it will be seen that the absolute amount of borax evaporated in a given time is about the same in both cases, whether a large or a small quantity is used, indicating that the amount volatilized at a given high temperature depends chiefly on the surface of the fused mass.

In the following three experiments it was sought to determine in what form borax is volatile.

It is possible that either borax is volatile as such, or that it is dissociated at high temperatures, giving off  $B_2O_3$  and leaving  $Na_2O$  behind. An analysis of the residue after heating borax glass for a certain length of time would decide; for in case  $B_2O_3$  is evolved the percentage of  $Na_2O$  must be higher than if borax as such is volatilized. As the difference between the two values for  $Na_2O$  under the latter supposition would increase rapidly with the loss in weight, samples of borax glass were heated long enough to bring about a loss of some twelve per cent.

## III.

1.5630 grams  $Na_2B_4O_7 + 10H_2O$ , lost on heating 0.7380 gram  $H_2O = 47.21$  per cent. (Theoretical loss = 47.12 per cent.)

0.8250 gram borax glass remained and was heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
20	Crucible partly covered .....	0.0106	0.0106	1.3
20	Crucible covered, small space allowed, fine drops on lid .....	0.0020	0.0126	1.6
	The lid alone was heated .....	0.0060	0.0186	2.3
20	Crucible uncovered .....	0.0171	0.0357	4.4
60	Crucible uncovered .....	0.0365	0.0722	8.8
60	Crucible uncovered, heat less intense .....	0.0210	0.0932	11.34

0.8250 gram borax glass lost 11.34 per cent. in three hours.

The residue weighed 0.7318 gram, and was analyzed, yielding 0.2185 gram  $Na_2O$  or 29.85 per cent.

	Theory, if loss were $B_2O_3$ .	Theory, if loss were $Na_2B_4O_7$ .	Found.
$Na_2O$ .....	34.62 per cent.	30.69 per cent.	29.85 per cent.

## IV.

1.5691 grams  $Na_2B_4O_7 + 10H_2O$ , lost on heating 0.7387 gram  $H_2O = 47.07$  per cent. (Theoretical loss = 47.12 per cent.)

0.8304 gram borax glass remained and was heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
30	Crucible open .....	0.0134	0.0134	1.6
90	" " .....	0.0565	0.0699	8.4
35	" " .....	0.0220	0.0919	11.07
20	" " .....	0.0121	0.1040	12.52

0.8304 gram borax glass lost 12.52 per cent. in about three hours.

The residue weighed 0.7264 gram, and yielded on analysis 0.21796 gram  $\text{Na}_2\text{O}$ .

	Theory, if loss were $\text{B}_2\text{O}_3$ .	Theory, if loss were $\text{Na}_2\text{B}_4\text{O}_7$ .	Found.
$\text{Na}_2\text{O}$ .....	35.09 per cent.	30.69 per cent.	30.01 per cent.

The low results obtained for  $\text{Na}_2\text{O}$  in III and IV were found to be due to a slight loss liable to be incurred in the analytical process used (treatment with ammonium fluoride), which will be touched upon in a communication following this. This source of error was obviated in the following experiment :

## V.

0.9350 gram borax glass was heated as follows :

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
60	Crucible uncovered.....	0.0387	0.0387	4.1
120	" " .....	0.0914	0.1301	13.91

0.9350 gram borax glass lost 13.91 per cent. in three hours.

The residue weighed 0.8049 gram, and yielded on analysis 0.2439 gram  $\text{Na}_2\text{O}$ .

	Theory, if loss were $\text{B}_2\text{O}_3$ .	Theory, if loss were $\text{Na}_2\text{B}_4\text{O}_7$ .	Found.
$\text{Na}_2\text{O}$ .....	35.65 per cent.	30.69 per cent.	30.31 per cent.

These results show beyond doubt that borax is volatile as such, and are corroborated by the following observations :

A thin film of borax glass on the inside of a crucible can be entirely volatilized by persistent heating.

The drops which occasionally gather on the lid of the crucible in the experiments described, can also be driven off completely by continued heating.

## SUMMARY OF THE RESULTS OF EXPERIMENTS A, I-V.

Losses in per cent. at the end of	WEIGHTS OF BORAX GLASS.				
	I, 0.6532 gram.	II, 4.1845 grams.	III, 0.8250 gram.	IV, 0.8304 gram.	V, 0.9350 gram.
5 minutes.....	0.8	0.23	...	...	...
12 " .....	1.0	....	...	...	...
15 " .....	...	0.298	...	...	...
20 " .....	...	....	1.3	...	...
22 " .....	2.0	....	...	...	...
25 " .....	...	0.461	...	...	...
29 " .....	2.5	....	...	...	...
30 " .....	...	....	...	1.6	...
35 " .....	...	0.652	...	...	...

Losses in per cent at the end of	WEIGHTS OF BORAX GLASS.				
	I, 0.6532 gram.	II, 4.1845 grams.	III, 0.8250 gram.	IV, 0.8304 gram.	V, 0.9350 gram.
39 "	3.3	....	...	...	...
40 "	...	....	2.3	...	...
44 "	4.1	....	...	...	...
45 "	...	0.834	...	...	...
46 "	4.2	....	...	...	...
60 "	...	....	4.4	...	4.1
120 "	...	....	8.8	8.4	...
155 "	...	....	...	11.07	...
175 "	...	....	...	12.52	...
180 "	...	....	11.34	...	13.91

These values obtained for the volatility of borax at high temperatures suggested the study of the behavior of borax glass at a lower heat, with the following results:

#### B. VOLATILITY AT LOWER TEMPERATURES.

##### I.

4.0199 grams  $\text{Na}_2\text{B}_4\text{O}_{10} + 10\text{H}_2\text{O}$  were heated in a platinum crucible until the water was expelled and the weight was constant.

Water expelled = 1.887 grams = 46.96 per cent. (Theoretical loss = 47.12 per cent.)

2.1320 grams borax glass remained and were further heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time. gram.	Total loss, gram.	Total loss in per cent.
10	Bunsen burner with chimney, full flame .....	0.0000	0.0000	0.000
15	Moderate blast-flame, crucible half covered .....	0.0014	0.0014	0.065
15	Moderate blast-flame, crucible half covered, drops noticed on lid .....	0.0008	0.0024	0.112
20	Moderate blast-flame, crucible half covered, drops noticed on lid .....	0.0020	0.0044	0.206
5	Strong blast-flame, crucible open...	0.0048	0.0092	0.431
10	" " " " " " ...	0.0073	0.0165	0.774
60	Bunsen burner, full flame, crucible half covered .....	0.0000	0.0165	0.774

##### II.

2.4425 grams borax glass were heated for ten minutes over a strong blast-flame in order to insure perfect expulsion of water.



It weighed then 2.4327 grams and was further heated as follows :

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
30	Bunsen burner, strong flame, crucible half covered.....	0.0000	0.0000	0.000
15	Gentle blast-flame, crucible half covered.....	0.0015	0.0015	0.061
15	Gentle blast-flame, crucible half covered.....	0.0017	0.0032	0.131

### III.

0.6148 gram borax glass, after being heated for a short time over a strong blast-flame, weighed 0.6126 gram and was further heated as follows :

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
15	Stronger blast-flame, crucible half covered.....	0.0034	0.0034	0.555
15	Gentle blast-flame, crucible half covered.....	0.0016	0.0050	0.816
15	Gentle blast-flame, crucible half covered.....	0.0018	0.0068	1.110

### SUMMARY OF THE RESULTS OF EXPERIMENTS B, I-III.

Weight of borax glass.	Loss in per cent. at the end of			
	15 minutes, per cent.	30 minutes, per cent.	45 minutes, per cent.	50 minutes, per cent.
2.1320 grams.....	0.065	0.112	....	0.206
2.4327 " .....	0.061	0.131	....	....
0.6126 gram.....	0.555	0.816	1.110	....

The question here suggests itself how this behavior of borax might influence the accuracy of such determinations of boric acid as involve exposure of a borate to high temperatures, as for example in the determinations of boric acid by the methods of H. Rose and G. Schaffgotsch. (v. Fresenius Quant. Anal.)

As in these determinations borates of a higher basicity than borax are formed, the results just given, cannot be with certainty utilized, although the more basic borates are probably less volatile than borax. But even supposing these more basic borates to be as volatile as borax itself, a material error from this source can occur only, if there be but a small amount of the borate subjected to analysis, and if the expulsion of carbon dioxide be attempted at too high a temperature and maintained for an unduly long time.

To illustrate such an exceptional case let us refer for instance to the experiment under A I, where it is shown that 0.6532 gram borax glass lost in weight 0.0125 gram=two per cent., when exposed to a white heat for twenty-two minutes, while the crucible was uncovered for fifteen minutes.

If, therefore, 0.2805 gram boron trioxide be analyzed by the method of G. Schaffgotsch this amount would be equivalent to 0.6532 gram of the borate  $B_2O_3Na_2$  formed in this process; this salt would lose in weight two per cent. in twenty-two minutes, if exposed to a white heat, if we assume that it be exactly as volatile as borax under the same conditions.

There would then remain 0.6401 gram of the borate, containing 0.2749 gram of  $B_2O_3$ , which implies a loss of  $B_2O_3$  equal to 0.0056 gram or 1.99 per cent.

It is, however, evident from the above that a loss from volatilization of the borate will fall within the errors of manipulation, when in an analysis a normal amount of boric acid is taken, say not less than one gram and when the heating is maintained for about ten minutes at not too high a temperature. This is under the assumption that borates of a higher basicity than borax are volatile to the same extent as the latter. Whether this is the case or not I have not attempted to ascertain, but a preliminary experiment made with a borate of approximately the composition  $B_2O_3Na_2$  shows that an increase of basicity in the molecule of borax does not guard the more basic borate from volatilization entirely, for I observed with this borate the same phenomena noticeable when heating borax; *viz.*, the evolution of heavy vapors from its surface, implying a loss in weight when subjected to a white heat. A statement contrary to this fact was made by G. Schaffgotsch<sup>1</sup> in claiming that the salt formed by the action of one and a half molecules of  $Na_2CO_3$  on one molecule of  $B_2O_3$  [ $=B_2O_3Na_3$ ] is "gewichtsbeständig."

Prof. Karl Langenbeck, of Zanesville, Ohio, kindly consented to carry out some experiments on the volatilization of borax on a larger scale in kilns, making use of pyrometers. With the approval of Prof. Langenbeck, I herewith add his interesting

<sup>1</sup> G. Schaffgotsch, *Pogg. Ann.*, 107, 427. Ueber die Bestimmung der Borsäure und über die Flüchtigkeit der Borsäure.

communications on the subject which are in perfect accord with the results obtained in the laboratory.

I. JANUARY 30, 1894.

12.3036 grams of borax glass were placed in a small platinum dish and set in a fire-clay capsule four inches in diameter and four inches deep, and this placed next to the pyrometers of a kiln.

From incipient redness to the melting down of Seger's pyrometric cone No. 9, took about forty-eight hours when the firing was discontinued and the kiln allowed to cool, which in about twelve hours, was no longer red.

In other words the borax glass was at a red heat about sixty hours, and reached the temperature of the melting point of Seger's pyrometric cone No. 9, ( $=1410^{\circ}\text{C.}$ ). On removal from the kiln the inside of the clay capsule was heavily glazed and the borax glass in the platinum dish found to weigh 6.2776 grams, hence 6.0260 grams had been volatilized, or 48.98 per cent.

II. FEBRUARY 6, 1894.

5.7698 grams  $\text{Na}_2\text{B}_4\text{O}_{10}$ , exposed to the heat of Seger's pyrometric cone No. 7 ( $1350^{\circ}\text{C.}$ ) lost 1.2926 grams or 22.40 per cent. This heat took ten hours less to reach and cooled about two hours more quickly, hence the specimen was about twelve hours less under a red heat.

9.2036 grams  $\text{Na}_2\text{B}_4\text{O}_{10}$ , exposed to the heat of the melting point of an alloy fifteen per cent. Ag, eighty-five per cent. Au (about  $1050^{\circ}\text{C.}$ ) lost 0.7259 gram or 7.88 per cent.

To reach this heat from very low redness took about twenty hours, and the cooling to blackness six hours.

It looks very much as if it did not take so very much heat to begin the volatilization, and that the duration of fire rather than the temperature determines the amount of loss.

III. FEBRUARY 13, 1894.

7.5803 grams borax glass were exposed in a platinum dish to a heat, which was just sufficient to melt silver ( $954^{\circ}\text{C.}$ ) and by careful regulation of the gas this temperature was held, within very narrow limits for three hours.

The furnace is an up and down draught made by Geith, of Coburg, Germany, from designs of Seger, and has a zone of at least seventy-five cubic inches that is perfectly uniform in heat. The dish of borax glass and the pyrometric trials were placed in the center of this zone.

The dish lost in three hours 0.1115 grams or 1.47 per cent.

SUMMARY OF THE RESULTS OBTAINED BY PROF. LANGENBECK.

Amount of borax glass, grams.	Duration of heat, hours.	Maximum temperature.	Means of measuring the temperature?	Loss, grams.	Loss in per cent.
2.3036	60	1410° C.	Seeger's cone, No. 9.	6.0260	48.98
5.7698	48	1350° C.	Seeger's cone, No. 7.	1.2926	22.40
9.2036	26	1050° C.	Alloy 15 % Ag 85 % Au.	0.7259	7.88
7.5803	3	954° C.	Ag.	0.1115	1.47

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI. XLVI.]

ON THE VOLATILITY OF SODIUM FLUORIDE.<sup>1</sup>

BY SIGMUND WALDBOTT, PH.D.

THE analyses mentioned in Experiments A III and A IV of the foregoing communication did not at first give perfectly satisfactory results. In the endeavor to ascertain the cause of the deficiency, the analytical method employed was subjected to a careful examination.

This method, as described by A. Reischle,<sup>2</sup> is based on the principle that boric acid can be easily driven off from a borate by mixing it with six times its weight of resublimed ammonium fluoride, and heating carefully until all the boron is volatilized as ammonium borofluoride.

The residue, consisting of the fluorides of the metals that were combined with boric acid, is then treated with sulphuric acid and evaporated to dryness. The sulphates are ignited and weighed, and the amount of boric acid, if desired, is calculated from the difference between the original weight and the weight of the oxides present in the sulphates.

<sup>1</sup> Read before the Cincinnati Section, February 15, 1894.

<sup>2</sup> A. Reischle, *Ztschr. anorg. Chem.*, 4, 111-116. Abst. in *J. Chem. Soc.*, 1893, (abstracts) p. 491.

This process, according to comparative tests made by Reischle, has proved to be the best of all known methods for determining boric acid indirectly. Several analyses carried out in the laboratory of the University of Cincinnati confirm its reliability.

Experience shows, however, that a few precautions must be closely observed in order to insure accurate results.

The ammonium fluoride employed must be resublimed, or at least the residue left on sublimation must be carefully determined and the necessary deduction made from the final weighing.

Another source of possible error seemed to lie in the volatility of the alkaline fluorides at a comparatively low temperature, and some abnormal results recorded by Reischle, were probably due to this cause.

As nothing has been published on this subject it seemed desirable to examine closely the behavior of sodium fluoride, at least at varying temperatures, and bring the results of the study to bear upon the details of the Reischle method.

The sodium fluoride employed was chemically pure and procured from C. Schuchardt in Görlitz.

The following experimental results were obtained:

#### I.

NaF not dried, = 0.5605 gram.

Heated over the Bunsen burner, = 0.5495 gram.

Heated again for two minutes, = 0.5490 gram.

This weight, 0.5490 gram of dry NaF, was further heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
2	Moderate blast flame.....	0.0040	0.0040	0.71
6	Bunsen burner with chimney, crucible slightly uncovered.....	0.0020	0.0060	1.09
2	Blast-flame, crucible uncovered.....	0.0167	0.0227	4.1
12	Bunsen burner with chimney, crucible slightly uncovered.....	0.0060	0.0287	5.2

#### II.

NaF not dried, = 0.2775 gram.

Heated over Bunsen burner to constant weight, = 0.2714 gram.

This weight, 0.2714 gram of dried NaF, was further heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Loss in per cent.
6	Bunsen burner, crucible slightly uncovered .....	0.0039	0.0039	1.4
5	Bunsen burner, crucible slightly uncovered .....	0.0034	0.0073	2.7
5	Bunsen burner, lid off, contents half melted .....	0.0047	0.0120	4.4
10	Small flame, bottom just red hot, crucible slightly covered .....	0.0010	0.0130	4.9
15	Same, but flame slightly reduced ....	0.0003	0.0133	4.9

It follows from these experiments that the full flame of a Bunsen burner, if applied to 0.549 gram of sodium fluoride, will cause a loss of nearly 0.4 per cent. in six minutes, and if applied to 0.2714 gram will cause a loss of 1.4 per cent. in six minutes, while if the flame be reduced so that it will hardly redden the bottom of the covered platinum crucible there will be no very appreciable loss in fifteen minutes.

By observing these two precautions—subjecting sufficient material to analysis to yield not less than 0.6 gram sodium fluoride and applying as little heat as possible—the Reischle method gives excellent results, and the slight discrepancy between the results of the analysis in Experiment A V of the preceding paper, executed after the fact of the volatilization of sodium fluoride was ascertained, and the results of the analyses in experiments A III and A IV is readily accounted for.

In conclusion I wish to express to Prof. Norton my sincerest thanks for the many courtesies extended to me during these experiments. I feel likewise much indebted to Prof. Langenbeck for his kindness in having carried out the experiments on a larger scale as before recorded.

CINCINNATI, MARCH 21, 1894.

## ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND HENRY E. SPENCER.

Received May 5, 1894.

### I. SILVER FROM COPPER.

THE literature relating to electrolysis contains two suggestions bearing upon the separation of these metals. The first is that of Classen, (*Quantitative Analyse durch Elektrolyse, dritte Auflage*, p. 124). In reality this is not an electrolytic method

as the author proposes to first separate the metals by precipitating out the silver as oxalate, filtering off the same, dissolving it in potassium cyanide, and then decomposing this solution of the double cyanide of silver and potassium by means of the electric current. The double oxalate of copper and ammonium being soluble in water is filtered from off the insoluble silver oxalate, and the copper is then deposited from this solution by the current. No data obtained in the actual use of the method appear to have been published. The insolubility of silver oxalate in ammonium oxalate is not generally conceded (Rose, *Analyt. Chemie*, 1, 342), so that it might well be expected, if this statement be true, that the deposit of copper would contain silver. Experiments were instituted to ascertain how accurate the method really was. The results of a few are given below. They are at the least quite instructive.

*Experiment 1.*—Ten cc. of a cold saturated solution of ammonium oxalate were added to a solution containing fifty cc. of copper sulphate (= 0.2284 gram of metallic copper) and ten cc. of silver nitrate (= 0.1000 gram of metallic silver). The precipitated silver oxalate was filtered and washed with ten cc. of an ammonium oxalate solution and later with pure water. The washings were colorless and the filtrate was perfectly clear, not the slightest turbidity being observed. The liquid, now 200 cc. in volume, was heated to 50° C., and electrolyzed with a current of 3-4 cc. of electrolytic gas per minute. This procedure was as nearly like that prescribed by Classen (*Elektrolyse*, pp. 78, 124) as it could be, since that chemist fails to give details, leaving the same to the student for adjustment. The precipitation of the copper was rapid and in every respect satisfactory. The deposit of copper weighed 0.2285 gram. Apparently the separation was complete and in no way lacking. However, upon dissolving the copper in dilute nitric acid, diluting with water and adding dilute hydrochloric acid a decided cloudiness was produced. This was found to be *due to silver chloride*.

*Experiment 2.*—In this trial the quantity of copper was reduced to 0.1142 gram. The silver present equaled 0.1 gram. Twenty-five cc. of ammonium oxalate were used for the precipitation and eleven more for the washing. In other respects the

conditions were similar to those in Experiment 1. The copper deposit weighed 0.1140 gram, instead of 0.1142 gram as required by theory, *yet it contained a very decided amount of silver*, which was revealed upon examining the copper.

*Experiment 3.*—The details here were analogous to those in Experiment 1. The precipitated copper weighed 0.2283 gram, *but after solution gave 0.0012 gram silver chloride equal to 0.0009 gram metallic silver.*

*Experiment 4.*—This was similar to experiment 2. The precipitate of copper weighed 0.1134 gram. It was 0.0008 gram low, but notwithstanding it showed on examination the presence of 0.0009 gram of silver.

Many more trials were made with varying amounts of copper, silver, and ammonium oxalate, but in every instance silver showed itself upon examining the precipitated copper. The inevitable conclusion is then that, however insoluble silver oxalate may be in the absence of other metals when copper is present with it, weighable amounts do pass into solution. Care was taken not to electrolyze solutions that were not absolutely clear. At times great difficulty was experienced in getting a clear filtrate from the silver oxalate. All cloudy filtrates were rejected. The results given above demonstrate that the suggestion of Classen (*loc. cit.*) with reference to the separation of silver and copper is not entitled to any consideration on the part of those who are engaged in electrolytic studies.

From an article published in the *Ztschr. angew. Chemie*, 696 (1892), by Rüdorff, it would seem that this chemist also failed, in using Classen's method, to obtain satisfactory results. The experiments in this communication are, therefore offered as a confirmation of Rüdorff's observations so far as concerns the separation of silver and copper.

The second suggestion in regard to the electrolytic separation of these two metals was offered by Smith and Frankel (*J. Frank. Inst.*, 1889; Smith's *Electrochemical Analysis*, p. 100). They electrolyzed a solution containing the double cyanides in the presence of an excess of alkaline cyanide. Numerous repetitions of their method, made in this laboratory, confirm their observation. Rüdorff (*loc. cit.*) also found it satisfactory. The time-



factor can, as will be noticed below, be much reduced by merely electrolyzing the solution at a temperature ranging from 65° to 70° C. The method in consequence is rendered more serviceable. Results obtained in this way follow:

*Experiment 1.*—A solution under electrolysis contained 0.1 gram of metallic silver and 0.1140 gram of metallic copper. The quantity of potassium cyanide present equaled 1.8 grams. The temperature of the liquid was maintained at 65° C., throughout the entire decomposition. The current was  $N.D_{100}=0.07$  ampere. The total dilution of the solution equaled 200 cc. The time required for the complete precipitation of the silver was about three hours. The deposit weighed 0.0996 gram; it did not contain copper.

*Experiment 2.*—In this trial the conditions were similar to those in Experiment 1. The silver deposit weighed 0.1 gram. It contained no copper.

A silver dime was dissolved and the solution diluted to a definite volume. Twenty-five cc. of this solution contained 0.1081 gram of metallic silver. One gram of potassium cyanide was added to the solution and the whole then diluted to 200 cc. The temperature of the liquid during the electrolysis was 60° C. The time of precipitation occupied three hours. The silver deposit weighed 0.1080 gram; it was free from copper.

Fifty cc. of the coin solution ( $=0.2162$  gram of metallic silver) were mixed with two grams of potassium cyanide, diluted with water to 225 cc., heated to 65° C., and electrolyzed with a current of  $N.D_{100}=0.07$  ampere. The precipitated silver weighed 0.2153 gram.

The method of Smith and Frankel, as thus modified is applicable where results are desired in a comparatively short time-period.

## 2. MERCURY FROM COPPER.

These metals were also fully separated from each other by the electrolytic decomposition of their double cyanide solution (Smith and Frankel, *Am. Chem. J.*, **11**, 264, 104; Smith and McCauley, *J. Anal. Appl. Chem.*, **5**, 489, and *Ber. d. chem. Ges.*, **24**, 2936; also Freudenberg, *Ztschr. phys. Chem.*, **12**, 113). No difficulty attends the separation, and possibly the only objection

that could be offered to the method is, that considerable time is required for its completion. As in the case of silver and copper it is only necessary to apply a gentle heat to the solution undergoing electrolysis and the time-factor will be greatly reduced. For example:

*Experiment 1.*—A solution of 200 cc. volume, containing 0.2167 gram of metallic mercury, 0.2156 gram of metallic copper, and two grams of potassium cyanide was heated to 65° C. and electrolyzed with a current of  $N.D_{100} = 0.08$  ampere. The precipitation was finished in three and one-half hours. The deposit of mercury was adherent and weighed 0.2168 gram. It contained no copper.

*Experiment 2.*—Here the conditions were nearly like those in (1). The current of  $N.D_{100} = 0.06$  ampere acted for a period of four hours. The precipitated mercury weighed 0.2169 gram, but it did not contain copper.

*Experiment 3.*—The temperature of the solution was 70° C. The current of  $N.D_{100} = 0.08$  ampere acted through four hours. The mercury weighed 0.2170 gram. It contained no copper.

*Experiment 4.*—In this trial the quantity of each metal was half the amount given in the preceding experiments. But one gram of potassium cyanide was present. The current of  $N.D_{100} = 0.08$  ampere acted three hours upon the solution heated to 70° C. The precipitated mercury weighed 0.1083 gram. Copper was not found in it.

### 3. SILVER FROM CADMIUM.

These metals have usually been separated electrolytically when present in nitric acid solution. As both are precipitated by rather feeble currents from solutions containing them as double cyanides, it did not occur to the writers until recently that they could also be separated from each other in a solution of this nature. The two experiments which follow show that such is indeed the case. The separation cannot be made in a cold solution. The silver will always be contaminated with cadmium. The most favorable conditions are noted in the examples here given.

*Experiment 1.*—A solution of 200 cc. volume contained 0.1000 gram of metallic silver, a like quantity of metallic cadmium, and

three grams of potassium cyanide. It was heated to  $65^{\circ}$  and then electrolyzed for three and one-half hours with a current of  $N.D_{100} = 0.04$  ampere. The precipitated silver weighed 0.1004 gram. No cadmium was found in it. The poles were separated two inches from each other.

*Experiment 2.*—Operating with conditions just like those in experiment 1, the deposit of silver weighed 0.0999 gram.

UNIVERSITY OF PENNSYLVANIA,  
April 23, 1894.

## THE ACTION OF PHOSPHORUS PENTACHLORIDE UPON MOLYBDENUM TRIOXIDE.

BY EDGAR F. SMITH AND GEORGE W. SARGENT.

Received May 5, 1894.

THE action of phosphorus pentachloride upon the trioxides of tungsten and of molybdenum has been the subject of investigation by Schiff,<sup>1</sup> Teclu,<sup>2</sup> and Piutti.<sup>3</sup> Schiff announced that with tungstic acid and the pentachloride the products were in the main phosphorus oxychloride and a brown colored tungsten oxychloride. Teclu, upon repeating Schiff's experiments, obtained phosphorus oxychloride and the *hexachloride of tungsten*. This was the result when working with one part of  $WO_3$  and three parts of phosphorus pentachloride. The mixture was heated in sealed tubes. Piutti substituted molybdenum trioxide and hoped to get a corresponding molybdenum *hexachloride*. This he did not realize; instead, he obtained a compound which gave results on analysis that led to the formula  $MoCl_3 \cdot POCl_3$ . Along with the dark-green colored crystals of this compound there was a reddish-brown liquid. The tube, after being opened, and as soon as the liquid was removed, was connected with a Woulff bottle to which a drying tube was attached. The other end of the sealed tube was opened and connected with a carbon dioxide generator. The tube was next surrounded with water at  $80^{\circ}$ , and a current of carbon dioxide conducted through it, when the green colored crystals sublimed. They were carefully collected and gave the results from which was deduced the formula given above. We have repeated the experiment of Piutti under

<sup>1</sup> *Annalen der Chemie*, 100, 115.

<sup>2</sup> *Annalen der Chemie*, 187, 255.

<sup>3</sup> *G. ch. italiana*, 9, 538.

slightly modified conditions. Thus, we exposed 1.5 grams molybdenum trioxide and ten grams of phosphorus pentachloride in a sealed tube, filled with chlorine, to a temperature of  $175^{\circ}\text{C}$ . The sides of the tube, on cooling, were covered with greenish-black crystals. One end of the tube was broken open, quickly connected with a dry flask, after which the other end was opened and attached to a delivery tube in union with a chlorine generator. As the chlorine gas was conducted through the tube a gentle heat was applied to the latter, when a colorless liquid distilled over and was carefully collected. Later the greenish-black crystals sublimed and were collected separately in a dry vessel. The analysis of the colorless liquid just mentioned indicated it to be phosphorus oxychloride. The greenish-black solid was rapidly weighed out in weighing bottles. The vessel containing the portion intended for the chlorine determination was, after weighing, uncorked under water and the substance allowed to gradually enter the water. The disengaged gases were thus wholly absorbed.

*Chlorine Determinations.*—(1) 0.3702 gram substance gave 1.0881 gram silver chloride, equal to 0.2720 gram chlorine, or 73.47 per cent. (2) 0.3103 gram substance gave 0.9074 gram silver chloride, equal to 0.2268 gram chlorine, or 73.14 per cent.

*Phosphorus Determinations.*—(1) 0.5610 gram substance gave 0.1375 gram magnesium pyrophosphate, equivalent to 6.84 per cent. phosphorus. (2) 0.7991 gram substance gave 0.1914 gram magnesium pyrophosphate, equal to 6.67 per cent. phosphorus.

*Molybdenum Determination.*—The substance was digested with ammonium sulphide, and from this solution hydrochloric acid precipitated the trisulphide, which was changed to disulphide and weighed as such. 0.2385 gram material gave 0.0457 gram, equal to 19.17 per cent. Mo.

From these figures we deduce an atomic ratio, which would point to our compound as being a union of one molecule of molybdenum pentachloride with one molecule of the phosphorus haloid— $\text{MoCl}_5 \cdot \text{PCl}_5$ . The theoretical percentages in this case are:

Mo = 19.91 per cent., Cl = 73.65 per cent., P = 6.43 per cent.

Our compound is greenish-black in color and decomposes

quite easily. The conditions under which we operated being slightly different from those of Piutti, it is not surprising that our product should be different. We used an excess of the phosphorus haloid and took care that the tube in which the reaction occurred contained chlorine gas. Subsequently we also distilled out the phosphorus oxychloride in a current of chlorine, and did not use carbon dioxide until after the removal of the liquid, and not while the tube was exposed to a gentle heat. The reaction which occurred with us may be, perhaps, represented as follows:



With even a larger excess of the phosphorus haloid the same product was found, so that it is hardly probable that we can hope to arrive at the hexachloride of molybdenum through this reaction.

UNIVERSITY OF PENNSYLVANIA,  
April 26, 1894.

## SEPARATION OF TITANIUM FROM IRON.

BY CHARLES BASKERVILLE.

Received April 16, 1894.

IN the recent literature which I have been able to consult, the separation of titanium from iron by means of sulphurous acid, has been confined to the sulphates of these two metals. This process is long and tedious and often unsatisfactory.

If a neutralized solution of titanium and iron chlorides, of not too great dilution, be boiled with an excess of sulphurous acid, the iron becomes deoxidized at once and a white flocculent precipitate of titanium settles out. By this means the titanium is obtained free from iron and requires no re-solution and second precipitation, as is frequently necessary for purification when precipitated from the sulphate. If the sulphate be changed into a chloride by precipitation with ammonium hydroxide and dissolving again in dilute hydrochloric acid and neutralizing the excess of acid with ammonium hydroxide, the separation is easily effected. The accuracy of the method is shown by the two following analyses:

	Found.	Used.
TiO <sub>2</sub> .....	0.0322	0.0308
TiO <sub>2</sub> .....	0.0317	0.0314

The tedious boiling with sulphurous acid is avoided. A clean precipitate, which settles well and does not cling tenaciously to the sides and bottom of the beaker, filters rapidly and easily washed with hot water, is obtained. Salts of aluminum remain in solution.

UNIVERSITY OF NORTH CAROLINA.

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### NEW BOOKS.

**THE TANNINS.** A MONOGRAPH ON THE HISTORY, PREPARATION PROPERTIES, METHODS OF ESTIMATION AND USES OF THE VEGETABLE ASTRINGENT, WITH AN INDEX TO THE LITERATURE OF THE SUBJECT. BY HENRY TRIMBLE, Ph.M. Volume 2, pp. 172. Philadelphia: J. B. Lippincott & Co. 1894. Price, \$2.

The first volume of this work which appeared in 1892, was devoted to a general consideration of the subject and to gallo-tannic acid. The present volume deals primarily with the technically important tannins from the several species of oak bark and in a minor degree with those from mangrove, canaigre, and chestnut.

The tannins are usually dismissed by the chemist with the statement that they belong to a class of compounds about which very little is known and a few qualitative reactions at most, are given as characterizing them. Nevertheless they are of such importance that every one should know something of them. The author has endeavored to make an understanding of them possible by suggesting in some introductory remarks a method of study in which it is recommended to first investigate the sources of a tannin, then its history, method of preparation, properties, and finally a process for estimating it. It is usual for a chemist to begin with the last one of these; namely, the method of estimation and the result is invariably a failure.

With the exception of the historical chapters, this volume is made up almost entirely of the results of original research and the results of this work may best be understood by quoting from the final chapter, entitled Conclusions. "In looking over the composition of these tannins discussed in the volume, and comparing them with what appeared to be trustworthy results obtained in recent years by other investigators, we find that they

all arrange themselves according to their percentage of carbon and hydrogen into the following two groups :

	I. The gallo- tannin group.	II. The oak- tannin group.
Carbon.....	52.17 per cent.	60.00 per cent.
Hydrogen.....	3.10 " "	5.00 " " "

The tannins from nutgalls, chestnut wood and bark, pomegranate bark and sumac are classified under the first group, while those from oak bark, mangrove, canaigre, rhatany, kino, catechu, and tormentil, are found to fall within the limit of the second group.

This is nearly the old classification of "iron-blueing" and "iron-greening" tannins, but we believe with this important difference that oak-tannins so far as investigated give a green with salts of iron and not a blue as usually stated in the books. The blue color with salts of iron, the author claims, is obtained only with infusions of oak bark, and this is due to the presence of an iron-blueing coloring matter which accompanies the tannins.

S. P. S.

A SYSTEM OF INSTRUCTION IN QUALITATIVE CHEMICAL ANALYSIS. BY ARTHUR H. ELLIOTT, PH.D., published by the author. N, Y. 1894. Price \$2.00.

This treatise on qualitative analysis is neat in general appearance, printed in clear type and the nomenclature used is good. There is one feature of it; namely, the almost entire absence of equations representing the nature of reactions, which will bear criticism. It is impossible without a most elaborate system of experiments performed before the study of qualitative analysis is begun, to make students so familiar with the nature of chemical reactions, that these can be entirely neglected. Moreover, the average instructor of the subject prefers to keep the reactions constantly before the student as would be the case if they were introduced into the text.

It is easy to understand why such a treatise might be adopted by those engaged in the teaching of students of pharmacy and medicine, as the latter seldom enter deeply enough into the subject to consider the exact nature of the reactions involved. While leaving equations to be explained by the instructor

many minor points of manipulation are treated at unnecessary length. These might have been explained once for all beforehand.

A good feature is the mention of the occurrence in nature and in commerce of compounds of the element under discussion, a feature which is often ignored in books of its scope.

The chapters on the separations and detection of acids and bases are well written.

FRED'K W. SPANUTIUS.

"THERMODYNAMICS OF REVERSIBLE CYCLES IN GASES AND SATURATED VAPORS." BY M. I. PUPIN, PH.D.; edited by Max Osterberg. 114 pp. New York: John Wiley & Sons. 1894.

This little volume contains a "full synopsis of a ten weeks' undergraduate course of lectures," arranged (with the author's sanction) by a student of Columbia College. The course is designed as a theoretical introduction to a practical course in heat engines, not to a general course in physical chemistry. The Calculus is used throughout, but the mathematical notation is somewhat relieved by illustrations. The two laws are discussed successively with reference to perfect gases and Carnot's cycle. The integral and the differential equations of the indicator diagram are quite happily compared to Kepler's laws of planetary orbits as a whole, and Newton's successful analysis of these orbits into their minutest parts under the law of gravitation.

Steam is taken as the familiar type of saturated vapors; special emphasis is placed on the discussion of adiabatic and isothermal expansion; and reasons are given that the prevailing types of steam engines are not strictly reversible.

R. B. W.

SELECT TABLES FROM THE U. S. PHARMACOPOEIA, 1890. REPRINTED FOR READY REFERENCE IN DAILY PRACTICE. Published by the Committee of Revision. Philadelphia: Agents, P. Blakiston, Son and Company. 1893.

The list comprises: Alphabetical List of Volumetric Assays; Alcoholometric Table, according to E. R. Squibb; Saturation Tables; Equivalents of Weights and Measures, customary and metric; Table of Thermometric Equivalents; List of the Prin-



cial Pharmacopoeial Chemicals and Reagents, with their molecular weights; and Table of Atomic weights, according to L. Meyer and K. Seubert.

These respective tables are on 8vo. heavy paper for mounting on cardboard and hanging in the office or laboratory.

While the chemist may not use the whole Pharmacopoeia, these tables are just that part which will be found very useful to him. We cannot refrain from suggesting, however, that the practical chemist would make no mistake in familiarizing himself with the chemical portions of the whole book.

H. T.

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#### NOTES.

*Preparation of Standard Iodine Solutions.*—The usual directions given for the preparation of standard solutions of iodine, to grind in a mortar, with a small quantity of water, the proper proportions of iodine and potassium iodide, transfer to the graduate-vessel and dilute, may be improved upon, both as to time required and danger of accidental loss of material, by the following method :

Iodine and potassium iodide, in the ratio of about two to three respectively, are carefully transferred to a graduate-flask and a weight of water added not greater than the weight of iodine used. The flask is then to be shaken until the scales of iodine disappear, care being taken not to splash the solution upon the stopper of the vessel. The required dilution is best made slowly with constant shaking. Three to five minutes are usually sufficient for the preparation of the solution and the rapidity and ease with which it may be accomplished largely depends upon using a minimum amount of water at first.

February 6, 1894.

DAVID HANCOCK.

*Meeting of the Association of Official Agricultural Chemists.*—The Executive Committee of the Association of Official Agricultural Chemists has decided to call the Annual Meeting of the Association for August 23, 24, and 25, 1894. The meetings will

be held in the Lecture Room of the National Museum, at Washington, D. C., beginning at 10 o'clock on Thursday, August 23.

The reporters for the meeting are as follows: Phosphoric acid—B. W. Kilgore, Raleigh, N. C. Nitrogen—J. M. Bartlett, Orono, Me. Potash—H. J. Wheeler, Kingston, R. I. Soils and ash—A. M. Peter, Lexington, Ky. Dairy products—F. H. Farrington, Champaign, Ill. Foods and feeding stuffs—H. J. Patterson, College Park, Md. Fermented liquors—Geo. F. Colby, Berkeley, Cal. Sugar—G. L. Spencer, Washington, D. C.

The co-operation of European chemists has been invited in the analytical work and several acceptances of the invitation have been received. It is urged upon all members who have communications to make to the Association to bring them properly prepared and ready for printing. Much delay has arisen heretofore in securing the manuscript promptly from the reporters and others presenting papers. The speedy publication of the proceedings will be greatly facilitated by bringing everything properly prepared.

H. W. WILEY, *Sec'y.*

*The Assimilation of Free Nitrogen.*—On page thirty of the January number of this JOURNAL I spoke of the activity of a germ which assimilated free nitrogen, attributing the discovery to Winogradsky and Warington. Mr. Warington writes me that he is not entitled to any credit for this discovery and on re-reading the original article in *The Chemical News* I find that he only called attention to its activity. The mistake arose from the intimate association in my mind of Mr. Warington's name with the researches into the nature of nitrifying organisms. I make this correction at the request of Mr. Warington.

H. W. Wiley.















